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Selected scientific information through early 1986 is presented and evaluated relative to the health and welfare effects associated with exposure to ozone and other photochemical oxidants.

Data on health and welfare effects are emphasized; additional information is provided for understanding the oxidant pollution problem, for evaluating the reliability of effects data, and for assessing effects data relative to concentration occurring in ambient air. Information is also presented on exposure-related topics: sources, measurement, and concentrations of oxidant precursors; formation and transport of ozone and other photochemical oxidants; properties, chemistry, and measurement of ozone and other photochemical oxidants; and the concentrations of ozone and other photochemical oxidants typically found in ambient air.

The specific areas addressed by chapters on health and welfare effects are the toxicological appraisal of effects of ozone and other oxidants; effects observed in controlled human exposures; effects observed in field and epidemiological studies; and effects on vegetation, natural and agroecosystems, and nonbiological materials.

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Volume II of V

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ABSTRACT

Scientific information is presented and evaluated relative to the health and welfare effects associated with exposure to ozone and other photochemical oxidants. Although it is not intended as a complete and detailed literature review, the document covers pertinent literature through early 1986.

Data on health and welfare effects are emphasized, but additional information is provided for understanding the nature of the oxidant pollution problem and for evaluating the reliability of effects data as well as their relevance to potential exposures to ozone and other oxidants at concentrations occurring in ambient air. Information is provided on the following exposure-related topics: nature, source, measurement, and concentrations of precursors to ozone and other photochemical oxidants; the formation of ozone and other photochemical oxidants and their transport once formed; the properties, chemistry, and measurement of ozone and other photochemical oxidants; and the concentrations of ozone and other photochemical oxidants that are typically found in ambient air.

The specific areas addressed by chapters on health and welfare effects are the toxicological appraisal of effects of ozone and other oxidants; effects observed in controlled human exposures; effects observed in field and epidemiological studies; effects on vegetation seen in field and controlled exposures; effects on natural and agroecosystems; and effects on nonbiological materials observed in field and chamber studies.

AIR QUALITY CRITERIA FOR OZONE
AND OTHER PHOTOCHEMICAL OXIDANTS

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LIST OF ABBREVIATIONS AND SYMBOLS

~	approximately
λ	wavelength
AFR	air:fuel ratio
APHA	American Public Health Association
aq	aqueous
AGL	above ground level
ASL	above sea level
atm	atmosphere
avg	average
b.p.	boiling point
bz	benzene
C	carbon
°C	degrees Celsius
CA	chromotropic acid
CAMP	Continuous Air Monitoring Program
CARB	California Air Resources Board
cc	cubic centimeter
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
cm	centimeter
concn	concentration
DBH	tree diameter at breast height
DNPH	2,4-dinitrophenylhydrazine
DOT	Department of Transportation
E°_{0}	normal electrode potential
ECD	electron-capture detector
EKMA	Empirical Kinetic Modeling Approach
EPA	U.S. Environmental Protection Agency
EST	eastern standard time
FID	flame ionization detector
FRM	Federal Reference Method
ft	foot

LIST OF ABBREVIATIONS AND SYMBOLS
(continued)

FTIR	Fourier-transform infrared
g	gram(s)
g/mi	grams per mile
GC	gas chromatography
GMT	Greenwich mean time
GPT	gas-phase titration
hr	hour(s)
hv	photon
HC	hydrocarbons
HCN	hydrogen cyanide
HCOOH	formic acid
HFET	Highway Fuel Economy Driving Schedule
Hg	mercury
H_2O_2	hydrogen peroxide
HO_2	hydroperoxy
HONO	nitrous acid
$HONO_2$	nitric acid
HPLC	high-pressure liquid chromatography; also, high-performance liquid chromatography
HPPA	3-(p-hydroxyphenyl)propionic acid
HRP	horseradish peroxidase
H_2O	water
H_2SO_4	sulfuric acid
in	inch(es)
IR	infrared
k	constant
KI	potassium iodide
km	kilometer
L	liter(s)
LAAPCD	Los Angeles Air Pollution Control District
LCV	leuco crystal violet
ln	natural logarithm (base e)
LST	local standard time

LIST OF ABBREVIATIONS AND SYMBOLS
(continued)

M	molar
m	meter(s)
mb	millibar(s)
MBTH	3-methyl-2-benzothiazolinone hydrazone
mg	milligram(s)
mg/m^3	milligrams per cubic meter
MGE	modified graphite electrode
min	minute(s)
ml	milliliter(s)
mm	millimeter(s)
mM	millimolar
MMC	mean meridional circulation
m.p.	melting point
mph	miles per hour
MS	mass spectrometry
MSL	mean sea level
MTBE	methyl tertiary butyl ether
NA	not available
NAAQS	National Ambient Air Quality Standard
NADB	National Aerometric Data Bank
NAMS	National Aerometric Monitoring Stations
NAPBN	National Air Pollution Background Network
NAS	National Academy of Sciences
NBS	National Bureau of Standards
NECRMP	Northeast Corridor Regional Modeling Project
NEDS	National Emissions Data System
NEROS	Northeast Regional Oxidant Study
NH_3	ammonia
NH_4NO_3	ammonium nitrate
NF	National Forest
nm	nanometer(s)
NMHC	nonmethane hydrocarbons
NMOC	nonmethane organic compounds

LIST OF ABBREVIATIONS AND SYMBOLS
(continued)

NO	nitric oxide
NO_x	nitrogen oxides
NO_2	nitrogen dioxide
NO_3	nitrogen trioxide
N_2O	nitrous oxide
NR	natural rubber
NYCC	New York City Driving Schedule
O_2	oxygen
O_3	ozone
PAN	peroxyacetyl nitrate
PBzN	peroxybenzoyl nitrate
PNA	peroxynitric acid
PPN	peroxypropionyl nitrate
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PSD	Prevention of Significant Deterioration
psig	pounds per square inch gauge
PST	Pacific standard time
PUFA	polyunsaturated fatty acids
RAPS	Regional Air Pollution Study
RTI	Research Triangle Institute
S.D.	standard deviation
SAROAD	Storage and Retrieval of Aerometric Data
SBR	styrene-butadiene rubber
SCAB	South Coast Air Basin
sec	second(s)
SLAMS	State and Local Air Monitoring Stations
SMSA	Standard Metropolitan Statistical Area
SRM	Standard Reference Material
SSET	small-scale eddy transport
STA	seasonal tropopause adjustment
STP	standard temperature and pressure

LIST OF ABBREVIATIONS AND SYMBOLS
(continued)

SURE	Sulfate Regional Experiment Sites
TEL	tetraethyl lead
Tenax GC	adsorbent used in NMOC analysis
TF	tropopause-folding events
Tg/yr	teragrams per year
THC	total hydrocarbon
TML	tetramethyl lead
TNMHC	total nonmethane hydrocarbons
TWC	three-way catalyst
$\mu g/m^3$	microgram(s) per cubic meter
μM	micromolar
U	uranium
UHAC	uranium hydroxamic acid chelates
U.S.	United States
UV	ultraviolet
V	vanadium
v/v	volume-volume
VHAC	vanadium hydroxamic acid chelates
VOC	volatile organic compounds
vol %	volume percent
w/w	weight-weight
WCOT	wall-coated open tubular (column)
XAD-2	absorbent used in NMOC analysis
XO	xylenol orange
yr	year(s)

Chapter 3:

Principal Authors

*Mr. Thomas B. McMullen
Environmental Criteria and Assessment Office
MD-52
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

*Mr. Elmer Robinson
Director, Mauna Loa Observatory
National Oceanic and Atmospheric Administration (NOAA/CMCC)
Hilo, HI 96720

*Ms. Beverly E. Tilton
Environmental Criteria and Assessment Office
MD-52
Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Halvor Westberg
Director, Laboratory for Atmospheric Research, and
Professor, Civil and Environmental Engineering
Washington State University
Pullman, WA 99164-2730

*Dr. Arthur M. Winer
Assistant Director
Statewide Air Pollution Research Center
University of California
Riverside, CA 92521

Contributing Authors

*Dr. A. Paul Altshuller
Atmospheric Sciences Research Laboratory
MD-59
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Basil Dimitriades
Atmospheric Sciences Research Laboratory
MD-59
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 3 Contributing Authors (cont'd.)

*Dr. Marcia C. Dodge
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. James M. Kawecki
TRC Environmental Consultants, Inc.
2001 Wisconsin Avenue, N.W.
Suite 261
Washington, DC 20007

*Dr. Harold G. Richter
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

The following people reviewed Chapter 3 at the request of EPA:

Dr. Joseph J. Bufalini
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Donald Fox
Associate Professor
Department of Environmental Science and Engineering
School of Public Health, 201H
University of North Carolina
Chapel Hill, NC 27514

Mr. Bruce Gay
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Eric Ginsburg
Office of Air Quality Planning and Standards
Control Programs Development Division
MD-15
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 3 Reviewers (cont'd.)

Mr. Gerald Gipson
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Robert Hall
Industrial Environmental Research Laboratory
MD-65
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Michael R. Kuhlman
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Mr. William A. Lonneman
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Chuck Mann
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. E. L. Martinez
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Edwin L. Meyer
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Johnnie Pearson
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 3 Reviewers (cont'd.)

Mr. Kenneth L. Schere
Atmospheric Sciences Research Laboratory
MD-80
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Stanley Sleva
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Divsion
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Chester W. Spicer
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Mr. Bruce Tichenor
Industrial Environmental Research Laboratory
MD-54
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

---

*Authors also reviewed portions of this chapter.

Chapter 4: Measurement of Ozone and Other Photochemical Oxidants and Their Precursors

Principal Authors

*Dr. Jimmie A. Hodgeson
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
26 W. St. Clair
Cincinnati, OH 45268)

*Mr. Michael W. Holdren
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Dr. M. Rene Surgi
Department of Chemistry
Louisiana State University
Baton Rouge, LA 70803

Contributing Authors

Dr. Sandor Freedman
Piedmont Technical Services
Hillsborough, NC 27278

*Ms. Beverly E. Tilton
Environmental Criteria and Assessment Office
MD-52
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

The following people reviewed Chapter 4 at the request of EPA:

Dr. A. Paul Altshuller
Atmospheric Sciences Research Laboratory
MD-59
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Joseph J. Bufalini
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 4 Reviewers (cont'd):

Dr. Donald Fox
Associate Professor
Department of Environmental Science and Engineering
School of Public Health, 201H
University of North Carolina
Chapel Hill, NC 27514

Mr. Bruce Gay
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. William A. Lonneman
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Kenneth Rehme
Environmental Monitoring Systems Laboratory
MD-77
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Harold G. Richter
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Stanley Sleva
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Chester W. Spicer
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Dr. Arthur M. Winer
Assistant Director
Statewide Air Pollution Research Center
University of California
Riverside, CA 92521

---

*Authors also reviewed portions of this chapter.

Chapter 5: Concentrations of Ozone and Other Photochemical Oxidants in Ambient Air

Principal Authors

*Mr. Thomas B. McMullen
Environmental Criteria and Assessment Office
MD-52
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

*Mr. Elmer Robinson
Director, Mauna Loa Observatory
National Oceanic and Atmospheric Administration (NOAA/CMCC)
Hilo, HI 96720

*Ms. Beverly E. Tilton
Environmental Criteria and Assessment Office
MD-52
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Contributing Author

Dr. Sandor Freedman
Piedmont Technical Services
Hillsborough, NC 27278

The following people reviewed Chapter 5 at the request of EPA:

Mr. Gerald Akland
Environmental Monitoring Systems Laboratory
MD-56
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Joseph J. Bufalini
Environmental Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Gary Evans
Environmental Monitoring Systems Laboratory
MD-56
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 5 Reviewers (cont'd):

Dr. Donald Fox
Associate Professor
Department of Environmental Science and Engineering
School of Public Health, 201H
University of North Carolina
Chapel Hill, NC 27514

Mr. Gerald Gipson
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Jimmie A. Hodgeson
Professor, Department of Chemistry
407 Choppin Hall
Louisiana State University
Baton Rouge, LA 70803

Mr. Michael W. Holdren
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Dr. Michael R. Kuhlman
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Mr. William A. Lonneman
Atmospheric Sciences Research Laboratory
MD-84
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Thomas McCurdy
Office of Air Quality Planning and Standards
Strategies and Air Standards Division
MD-12
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Edwin L. Meyer
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 5 Reviewers (cont'd):

Dr. Harold G. Richter
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
MD-14
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Chester W. Spicer
Battelle, Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Dr. Arthur M. Winer
Assistant Director
Statewide Air Pollution Research Center
University of California
Riverside, CA 92521

---

*Authors also reviewed portions of this chapter.

SCIENCE ADVISORY BOARD
CLEAN AIR SCIENTIFIC ADVISORY COMMITTEE

The substance of this document was reviewed by the Clean Air Scientific Advisory Committee of the Science Advisory Board in public sessions.

SUBCOMMITTEE ON OZONE

Chairman

Dr. Morton Lippmann
Professor
Department of Environmental Medicine
New York University Medical Center
Tuxedo, New York 10987

Members

Dr. Mary O. Amdur
Senior Research Scientist
Energy Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. Eileen G. Brennan
Professor
Department of Plant Pathology
Martin Hall, Room 213, Lipman Drive
Cook College-NJAES
Rutgers University
New Brunswick, New Jersey 08903

Dr. Edward D. Crandall
Professor of Medicine
School of Medicine
Cornell University
New York, New York 10021

Dr. James D. Crapo
Associate Professor of Medicine
Chief, Division of Allergy, Critical Care and Respiratory Medicine
Duke University Medical Center
Durham, North Carolina 27710

Dr. Robert Frank
Professor of Environmental Health Sciences
Johns Hopkins School of Hygiene and Public Health
615 N. Wolfe Street
Baltimore, Maryland 21205

Professor A. Myrick Freeman II
Department of Economics
Bowdoin College
Brunswick, Maine 04011

Dr. Ronald J. Hall
Senior Research Scientist and Leader
Aquatic and Terrestrial Ecosystems Section
Ontario Ministry of the Environment
Dorset Research Center
Dorset, Ontario
Canada POA1EO

Dr. Jay S. Jacobson
Plant Physiologist
Boyce Thompson Institute
Tower Road
Ithaca, New York 14853

Dr. Warren B. Johnson
Director, Atmospheric Science Center
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Dr. Jane Q. Koenig
Research Associate Professor
Department of Environmental Health
University of Washington
Seattle, Washington 98195

Dr. Paul Kotin
Adjunct Professor of Pathology
University of Colorado Medical School
4505 S. Yosemite, #339
Denver, Colorado 80237

Dr. Timothy Larson
Associate Professor
Environmental Engineering and Science Program
Department of Civil Engineering
University of Washington
Seattle, Washington 98195

Professor M. Granger Morgan
Head, Department of Engineering and Public Policy
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15253

Dr. D. Warner North
Principal
Decision Focus Inc., Los Altos Office Center, Suite 200
4984 El Camino Real
Los Altos, California 94022

Dr. Robert D. Rowe
Vice President, Environmental and Resource Economics
Energy and Resources Consultants, Inc.
207 Canyon Boulevard
Boulder, Colorado 80302

Dr. George Taylor
Environmental Sciences Division
P.O. Box X
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Dr. Michael Treshow
Professor
Department of Biology
University of Utah
Salt Lake City, Utah 84112

Dr. Mark J. Utell
Co-Director, Pulmonary Disease Unit
Associate Professor of Medicine and Toxicology in Radiation Biology and Biophysics
University of Rochester Medical Center
Rochester, New York 14642

Dr. James H. Ware
Associate Professor
Harvard School of Public Health
Department of Biostatistics
677 Huntington Avenue
Boston, Massachusetts 02115

Dr. Jerry Wesolowski
Air and Industrial Hygiene Laboratory
California Department of Health
2151 Berkeley Way
Berkeley, California 94704

Dr. James L. Whittenberger
Director, University of California Southern Occupational Health Center
Professor and Chair, Department of Community and Environmental Medicine
California College of Medicine
University of California - Irvine
19772 MacArthur Boulevard
Irvine, California 92717

Dr. George T. Wolff
Senior Staff Research Scientist
General Motors Research Labs
Environmental Science Department
Warren, Michigan 48090

PROJECT TEAM FOR DEVELOPMENT
OF
Air Quality Criteria for Ozone and Other Photochemical Oxidants

Ms. Beverly E. Tilton, Project Manager
and Coordinator for Chapters 1 through 5, Volumes I and II
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Norman E. Childs
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. J.H.B. Garner
Coordinator for Chapters 7 and 8, Volume III
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. Thomas B. McMullen
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. James A. Raub
Coordinator for Chapters 9 through 12, Volumes IV and V
Environmental Criteria and Assessment Office (MD-52)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. David T. Tingey
Coordinator for Chapter 6, Volume III
Environmental Research Laboratory
U.S. Environmental Protection Agency
200 S.W. 35th Street
Corvallis, OR 97330

2. INTRODUCTION

2.1 PURPOSE AND LEGISLATIVE BASIS OF THIS DOCUMENT

The Clean Air Act specifies that the Administrator of the United States Environmental Protection Agency (EPA) issue, and revise on a periodic basis, air quality criteria for certain air pollutants. Air quality criteria may be defined as qualitative and quantitative information that describes the effects of a pollutant on public health and welfare in terms of the respective exposures that elicited them. According to section 108 of the Clean Air Act, as amended in 1977, criteria shall

> ...accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of such pollutant in the ambient air, in varying quantities.
>
> (U.S.Code, 1982)

Air quality criteria provide the Agency with a scientific basis for deciding whether regulations controlling given pollutants are necessary and for deriving such ambient air quality standards as may be needed.

Among the air pollutants designated by the Administrator as criteria pollutants are those known as photochemical oxidants. This document is a revision of Air Quality Criteria for Ozone and Other Photochemical Oxidants (U.S. Environmental Protection Agency, 1978a). Its purpose is to review and evaluate the scientific literature on ozone and related oxidants and to document their effects on public health and welfare.

The term "photochemical oxidants" has historically been defined as those atmospheric pollutants that are products of photochemical reactions and that are capable of oxidizing neutral iodide ions (U.S. Environmental Protection Agency, 1978a). Research has established that photochemical oxidants in ambient air consist mainly of ozone, peroxyacetyl nitrate, and nitrogen dioxide, and of considerably lesser amounts of other peroxyacyl nitrates, hydrogen peroxide, alkyl hydroperoxides, nitric and nitrous acids, and formic acid. Other oxidants suspected to occur in ambient air but only in trace amounts include peracids and ozonides.

Although it is by definition a photochemical oxidant, nitrogen dioxide is not included among the oxidants discussed in this document. The formation of nitrogen dioxide clearly precedes the formation of ozone and other related oxidants in the ambient air. Thus, nitrogen dioxide is the dominant oxidant early in the day, while ozone and other related oxidants predominate from late morning or midday through much of the afternoon. Nitrogen dioxide is known to exert deleterious effects on human health and welfare. This fact, coupled with temporal and spatial variations in concentrations that differ from those of ozone and related oxidants, underlies the listing of nitrogen dioxide under section 108(a)(1) of the Clean Air Act as a criteria pollutant separate from ozone and other photochemical oxidants. The second criteria document prepared by EPA on the oxides of nitrogen was completed in 1982 (U.S. Environmental Protection Agency, 1982a). That document discussed nitric and nitrous oxides, nitrogen dioxide, nitric and nitrous acids, and nitrosamines. As used in this document, the term "photochemical oxidants" refers to ozone, the peroxyacyl nitrates, hydrogen peroxide, and formic acid. The oxides of nitrogen are discussed, but only in the context of their role as precursors to ozone and related oxidants.

2.2 THE OXIDANT PROBLEM

Ozone (O_3), a reactive allotrope of oxygen (O_2), occurs as a natural component of the atmosphere. It is found in its highest concentrations in the stratosphere, where it is formed through cyclic reactions resulting from the photolysis of oxygen into atomic oxygen and the subsequent reaction of atomic oxygen with other oxygen molecules.

Incursions of stratospherically produced ozone into the lower troposphere occur through meteorological and atmospheric exchange phenomena, resulting in a global background of ozone. To this global background of ozone of stratospheric origin are added ozone formed in the free troposphere and the contributions of ozone produced in the ambient air from photochemical reactions involving manmade emissions and natural products (e.g., natural emissions of volatile organic compounds). Manmade emissions of nitrogen oxides and volatile organic compounds are the chief contributors to the ozone burden found in the ambient air of urban areas. The presence of ozone in ambient air is the net result of various formation, stratospheric-tropospheric exchange, transport, and destruction processes.

Other photochemical oxidants occur in ambient air, but the nature and source of their global backgrounds are not well established. The additional photochemical oxidants of concern in this document, namely hydrogen peroxide, peroxyacetyl nitrate and its homologues, and formic acid, have, except for the latter, been detected in remote environments thought to be free of manmade influences; and all have been detected in the ambient air of urban areas.

The toxicity of ozone is well known. It is a strong oxidizing agent that is highly reactive with a wide spectrum of chemical moieties. Since ozone is a gas, studies of its health-related toxicity have centered largely on its capacity for affecting pulmonary function and the morphology of the respiratory tract, which is now well documented. In addition, its effects on extrapulmonary tissues and systems are also of concern and are the subject of some of the research discussed in this document. Studies of toxic effects of ozone on vegetation are also well documented and have focused on foliar injury and reduction in growth and yield. The toxicities of the peroxyacyl nitrates, of hydrogen peroxide, and of formic acid are less well documented than the toxicity of ozone, having been the focus of considerably less research because the levels at which these oxidants occur in the ambient air, even in urban areas, appear to warrant much less concern.

Ozone, but not the other oxidants mentioned above, is regulated under provisions and procedures spelled out in the Clean Air Act. Its concentrations in ambient air are controlled through the promulgation and attainment of primary and secondary national ambient air quality standards (NAAQS). As described in the Clean Air Act, criteria pollutants are those atmospheric pollutants that are ubiquitous and are emitted into the air from numerous and diverse sources. While widespread, ozone and the other photochemical oxidants found in ambient air are not emitted into the air as primary pollutants. Rather, they are formed as secondary pollutants in the atmosphere from ubiquitous primary organic and inorganic precursors that are emitted by a multiplicity of sources. Consequently, photochemical oxidant pollution in this country is the result of a combination of many factors, such as local meteorological conditions and the concentrations, composition, and patterns of occurrence of the primary pollutants that give rise to the oxidants.

2.3 SCOPE AND ORGANIZATION OF THIS DOCUMENT

The atmosphere does not easily lend itself to the partitioning required for documentation. Nevertheless, certain boundaries are logical for purposes of discussion as well as for purposes of regulatory decisions. Ozone and its organic precursors are known to give rise to secondary organic aerosols. Likewise, ozone and hydrogen peroxide both appear to participate in the atmospheric oxidation of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) to those inorganic aerosols leading to visibility degradation in the atmosphere and to acidic deposition. The contributions of ozone and hydrogen peroxide to the oxidation of NO_2 and SO_2 cannot be quantified at present, but are known to be minor compared to the oxidation of these compounds by hydroxyl radicals. In addition, ozone, the principal photochemical oxidant in ambient air, has no direct effects on visibility since, unlike NO_2 and SO_2, it does not absorb energy in the visible region of the spectrum. Thus, this document includes brief discussions, in Chapter 3, of the atmospheric chemistry of ozone and hydrogen peroxide relative to the formation of inorganic nitrogen and sulfur aerosols but does not include information on the actual effects associated with visibility degradation or acidic deposition. Since NO_2 and SO_2 are the immediate, direct precursors to the aerosol species involved, visibility degradation and acidic deposition are discussed in the respective air quality criteria documents on oxides of nitrogen and on particulate matter and sulfur oxides (U.S. Environmental Protection Agency, 1982a,b).

This document has been divided into five volumes for ease of review, printing, and distribution. Volume I consists of the summary and conclusions for the entire document. Volume II contains the introduction to the document (Chapter 2) and all chapters dealing with the formation, transport, and fate of photochemical oxidants (Chapter 3); the measurement of oxidants and their precursors (Chapter 4); and the concentrations of oxidants in ambient air (Chapter 5). Volume III contains the documentation of the effects of photochemical oxidants on vegetation, ecosystems, and nonbiological materials (Chapters 6, 7, and 8, respectively). Volume IV reviews the extensive body of data available on the toxicological effects of ozone and other oxidants in experimental animals and on *in vitro* effects on human cells and body fluids (Chapter 9). In Volume V, effects observed in human controlled exposures (Chapter 10) and in field and epidemiological studies (Chapter 11) are presented. In addition, that volume contains an evaluation of the health effects data of probable consequence for regulatory purposes (Chapter 12).

Neither control techniques nor control strategies for the abatement of photochemical oxidants are discussed in this document, although some of the topics included are relevant to abatement strategies. Technology for controlling the emissions of nitrogen oxides and of volatile organic compounds is discussed in documents issued by the Office of Air Quality Planning and Standards (OAQPS) of the U.S. Environmental Protection Agency (e.g., U.S. Environmental Protection Agency, 1978b, 1983). Likewise, issues germane to the scientific basis for control strategies, but not pertinent to the development of criteria, are addressed in numerous documents issued by OAQPS.

In addition, certain issues of direct relevance to standard-setting are not explicitly addressed in this document, but are addressed instead in documentation prepared by OAQPS as part of its regulatory analyses. Such analyses include: (1) discussion of what constitutes an "adverse effect," that is, the effect or effects the standard is intended to protect against; (2) assessment of risk; and (3) discussion of factors to be considered in providing an adequate margin of safety. While scientific data contribute significantly to decisions regarding these three issues, their resolution cannot be achieved solely on the basis of experimentally acquired information. Final decisions on items (1) and (3) are made by the Administrator.

A fourth issue directly pertinent to standard-setting is identification of the population at risk, which is basically a selection by the Agency of the population to be protected by the promulgation of a given standard. This issue is addressed only partially in this document. For example, information is presented in Chapter 12 on factors, such as pre-existing disease, that biologically may predispose individuals and subpopulations to adverse effects from exposures to ozone. The identification of a population at risk, however, requires information above and beyond data on biological predisposition, such as information on levels of exposure, activity patterns, and personal habits. Such information is included in a staff paper developed by OAQPS. Thus, the identification of the population at risk relative to standard-setting is the purview of OAQPS and is not addressed in this document. For information on the standard-setting process, see Padgett and Richmond (1983) and McKee et al. (1985).

This document consists of the review and evaluation of relevant literature on ozone and other photochemical oxidants through early 1986. The material selected for review and comment in the text generally comes from the more recent literature, with emphasis on studies conducted at or near pollutant concentrations found in ambient air. Older literature that was cited in the previous criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978) has often been summarized and presented briefly. An attempt has been made, however, to discuss at greater length in the text older studies (1) judged significant because of their usefulness in deriving the 1979 standards; (2) open to reinterpretation because of newer data; or (3) potentially useful in deriving subsequent standards. The newer information on oxidants now available may in some instances make possible a better understanding of the earlier studies, such that a more detailed and comprehensive picture of health effects is emerging on several issues. An attempt has been made to discuss key literature in the text and present it in tables as well. Reports of lesser importance to the purposes of this document may appear in tables only.

Generally, only published material that has undergone scientific peer review is included. In the interest of admitting new and important information, however, some material not published in the open literature but meeting other standards of scientific reporting may be included. Emphasis has been placed on studies in which exposure concentrations were ≤ 1 ppm. On this basis, studies in which the lowest concentration employed exceeded this level have been included only if they contain unique data, such as documentation of a previously unreported effect or of mechanisms of effects; or if they were multiple-concentration studies designed to provide information on concentration-response relationships. Application of a concentration cutoff of 1 ppm to health effects studies eliminates discussion of studies on mortality and sublethal effects. In the areas of mutagenesis, teratogenesis, and reproductive effects, however, results of studies conducted at much higher than ambient levels have been included because of the potential importance of these long-term effects to public health and welfare.

In selecting studies for consideration, each paper or other publication was reviewed in detail. Technical considerations for inclusion of a specific study on health or welfare effects, for example, included, but were not restricted to, an analysis of the exposure method; specificity or appropriateness of the analytical method used to monitor the oxidant concentration; information on oxidant monitoring practices such as location, calibration, and sampling time; and the appropriateness of the technique used to measure the effect. In addition, for health effects studies technical considerations included the characteristics of the subjects studied and the techniques used for obtaining or selecting the study cohorts. Interpretation of the results included consideration of the following factors: the end results of the statistical analysis; the degree to which the results are plausible in the context of other extant data; the appropriateness of the hypothesis developed; and the agreement between the hypothesis and the results reported. Unless otherwise stated, all results cited in the text for health and vegetation studies are statistically significant at $p \leq 0.05$.

The general policy of EPA is to express concentrations of air pollutants in metric units, e.g., in micrograms per cubic meter ($\mu g/m^3$); as well as in the more widely used units, parts per million (ppm) or parts per billion (ppb), which are neither metric nor English units. That policy has been followed in those chapters in which most of the data have been obtained from laboratory studies done at room temperature (e.g., Chapters 9 and 10). Data reported in ppm for studies conducted outdoors, such as field and open-top chamber vegetation studies, ambient air monitoring, and research on atmospheric chemistry, have not been converted. Conversion of reported ppm and ppb units is highly questionable in these cases because it assumes standard or uniform temperatures and pressures. For data in the health chapters, the conversion units used are 1 ppm ozone = 1962 $\mu g/m^3$, and 1 ppm PAN = 4945 $\mu g/m^3$; at 1 atmosphere pressure and 25°C.

2.4 REFERENCES

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3. PROPERTIES, CHEMISTRY, AND TRANSPORT OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS AND THEIR PRECURSORS

3.1 INTRODUCTION

Ozone and other oxidants found in ambient air, such as the peroxyacyl nitrates and hydrogen peroxide, are formed as the result of atmospheric physical and chemical processes involving two classes of precursor pollutants, volatile nonmethane organic compounds (NMOC) and nitrogen oxides (NO_x). The formation of ozone and other oxidants from these precursors is a complex, nonlinear function of many factors, including the intensity and spectral distribution of sunlight; atmospheric mixing and related meteorological conditions; the concentrations of the precursors in ambient air and, within reasonable concentration ranges, the ratio between NMOC and NO_x ($NMOC/NO_x$); and the reactivity of the organic precursors.

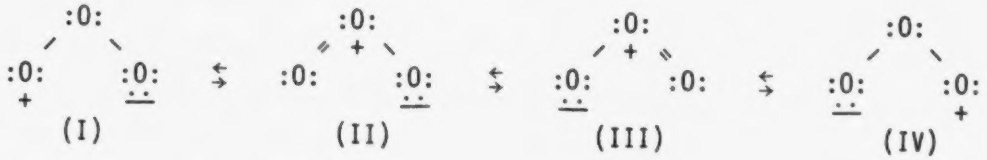
This chapter describes the physical and chemical properties of ozone and other photochemical oxidants (Section 3.2). It also characterizes the nature of the precursors in terms of their physical and chemical properties, their sources and emissions into the atmosphere, and their concentrations in ambient air (Section 3.5). In addition, a brief description is provided (Section 3.3) of the complex atmospheric chemical processes by which ozone and other photochemical oxidants are formed from their precursors. A brief discussion is also included of the relationship of ozone and other oxidants to atmospheric phenomena that result from the formation of secondary organic and inorganic aerosols.

In addition to the information on the chemistry of oxidants and their precursors, the chapter includes a discussion of meteorological processes (Section 3.4) that contribute to the formation of ozone and other oxidants and that govern their transport and dispersion once formed. Finally, an overview is given (Section 3.6) of models of source-receptor relationships between precursor emissions and ozone formation in the atmosphere, which either implicitly or explicitly include the relevant emissions, atmospheric chemistry, and meteorological processes.

3.2 DESCRIPTIONS AND PROPERTIES OF OXIDANTS AND THEIR PRECURSORS

3.2.1 Ozone and Other Photochemical Oxidants

3.2.1.1 Ozone. Ozone (O_3) is a triangularly shaped molecule consisting of three oxygen atoms arranged in four basic resonance structures:



The first and fourth structures, which predominate, are characterized by the presence of a terminal oxygen atom having only six electrons. The resonance forms depicted above have no unshared electrons. As the result of the presence of only six electrons on one of the oxygen atoms in ozone, the chemical reactions of ozone are electrophilic; that is, ozone removes electrons from or shares electrons with other molecules or ions. By definition, then, ozone is an oxidant since the term "oxidant" characterizes an ion, atom, or molecule that is capable of removing one or more electrons from another ion, atom, or molecule, a process called "oxidation." A "reducing agent" adds one or more electrons to another ion, atom or molecule, a process called "reduction." Oxidation and reduction reactions occur in pairs and the coupled reactions are known as "redox reactions." In redox reactions, the oxidizing agent is reduced and the reducing agent is oxidized. The two components of such redox reactions are known as "redox pairs." The significance of redox reactions involving ozone is discussed in Chapters 6 and 9. The capability of a chemical species for oxidizing or reducing is termed "redox potential" (positive or negative standard potential) and is expressed in volts. Ozone is, in fact, a strong oxidant having a standard potential of +2.07 volts in aqueous systems (Weast, 1977).

The physical properties of ozone are given in Table 3-1 (U. S. Department of Health, Education, and Welfare, 1970, modified).

TABLE 3-1. PHYSICAL PROPERTIES OF OZONE

Physical state	Colorless gas; blue violet liquid
Chemical formula	O_3
Molecular weight	48.0
Melting point	-192.7 ± 0.2°C
Boiling point	-111.9 ± 0.3°C
Specific gravity relative to air	1.658
Vapor density	
At 0°C, 760 mm Hg	2.14 g/liter
At 25°C, 760 mm Hg	1.96 g/liter
Solubility at 0°C (Indicated volume of ozone at 0°C, 760 mm Hg)	0.494 ml/100 ml water
Henry's Law constant, 37°C and pH = 7	8666 atm/mole fraction[a]
Conversion factors	
At 0°C, 760 mm Hg	1 ppm = 2141 $\mu g/m^3$ 1 $\mu g/m^3$ = 4.670×10^{-4}
At 25°C, 760 mm Hg	1 ppm = 1962 $\mu g/m^3$ 1 $\mu g/m^3$ = 5.097×10^{-4} ppm

[a] Calculated by formula of Roth and Sullivan (1981).

Source: U. S. Department of Health, Education, and Welfare (1970), modified.

3.2.1.2 Peroxyacetyl Nitrate. Peroxyacetyl nitrate (PAN) has been observed as a constituent of photochemical smog in many localities, though its concentrations and its ratio to ozone differ as a function of time at a given location as well as from place to place (Chapter 5). Peroxyacetyl nitrate, which has the formula $CH_3C(O)O_2NO_2$, exists in a temperature dependent equilibrium with its decomposition products, NO_2 and acetylperoxy radicals. It can persist for substantial periods of time in the atmosphere, depending upon temperature and the NO_2/NO ratio (Cox and Roffey, 1977).

The chief property of interest regarding PAN is its oxidizing ability. A second property of PAN of interest is its thermal instability. In the laboratory, this thermal instability necessitates that precautions be taken in synthesizing, handling and storing PAN, since improper handling and storage have resulted in explosions (Stephens et al., 1969). The ready thermal decomposition of PAN results in a notable temperature dependence in the rate of PAN decomposition in ambient air.

Partly because of the thermal instability of PAN, its properties have not been as well characterized as those of O_3 or H_2O_2. Recent work on the physical properties of PAN, however, has confirmed data reported earlier, and results of the earlier and more recent work are shown in Tables 3-2 and 3-3 (Stephens, 1969; U. S. Dept. of Health, Education, and Welfare, 1970; Kacmarek et al., 1978; Bruckmann and Willner, 1983; Holdren et al., 1984).

The infrared (IR) spectrum of PAN is important since most researchers rely on it for establishing concentrations of PAN for calibration. Bruckmann and Willner (1983) reported the IR spectrum of pure PAN and the Raman spectrum of liquid PAN at -40°C in an argon matrix. Their work confirmed effects that correlate with the ultraviolet (UV) spectrum published earlier by Stephens (1969); that is, PAN was shown to be stable at $\lambda > 300$ nm but was efficiently photolyzed at $\lambda < 300$ nm (Bruckmann and Willner, 1983). Actinic radiation falling upon the surface of the earth has wavelengths $\gtrsim 295$ nm, and it is light at wavelengths between ~295 and ~430 nm which is involved in photochemical air pollution formation.

3.2.1.3 Hydrogen Peroxide. Hydrogen peroxide (H_2O_2) is an oxidant that occurs in ambient air as a component of photochemical smog. It is believed to be formed through the recombination of two hydroperoxy radicals (HO_2) in the presence of a third, energy-absorbing molecule (section 3.3.1.3). In aqueous media, H_2O_2 is an inorganic acid that has a dissociation constant of 2.4×10^{-12} and a pK of 11.62 (at 25°C) (Weast, 1977). Hydrogen peroxide has a standard potential of +1.776 in the redox pair, H_2O_2/H_2O. The physical properties of H_2O_2 are given in Table 3-4.

Additional properties should be noted here that are of interest relative to whether effects of H_2O_2 in biological receptors are of significance. First, H_2O_2, though classed as a reasonably strong oxidant on the basis of its standard potential for the redox system H_2O_2/H_2O, has

TABLE 3-2. PHYSICAL PROPERTIES OF PEROXYACETYL NITRATE

Physical state, @25°C	Colorless liquid
Chemical formula	$CH_3COO_2NO_2$
Molecular weight	121
Boiling point, °C	106 ± 2[a] 103.9[b]
Triple point, °C	-50 ± 0.5[a] -48 ± 0.5[b]
Vapor pressure, @room temperature	~15 mm Hg
Vapor pressure curve	$\ln p = -4587/T + 18.76$[a,c] $\ln p = -4585/T + 18.79$[b]
Hydrolysis In alkaline solution	$t_{1/2} = 3.5$ min at pH = 7.8[d]; products include nitrite ion and molecular oxygen[e]
In acidic solution	
@22°C, pH 5.6	4×10^{-4} sec^{-1}[f]
@25°C, pH 5.6	6.8×10^{-4} sec^{-1}[g]
Henry's Law constant, @10°C	5 ± 1 M atm^{-1}[g]
Conversion factors	
@0°C, 760 mm Hg	1 ppm = 5398 $\mu g/m^3$ 1 $\mu g/m^3$ = 1.852×10^{-4} ppm
@25°C, 760 mm Hg	1 ppm = 4945 $\mu g/m^3$; 1 $\mu g/m^3$ = 2.022×10^{-4} ppm

Sources:

[a] Bruckmann and Wilner (1983).

[b] Kacmarek et al. (1978).

[c] Temperature, T, in °K; pressure, p, in torr.

[d] Mudd (1966).

[e] Stephens (1967); Nicksic et al. (1967).

[f] Lee et al. (1983).

[g] Holdren et al. (1984).

Source of remainder of data: U. S. Department of Health, Education and Welfare (1970).

TABLE 3-3. INFRARED ABSORPTIVITIES OF PEROXYACETYL NITRATE (RELATED TO 295°K and 973 mb) ($\text{ppm}^{-1}\ \text{m}^{-1} \times 10^4$) (base 10)

Reference	Frequency, cm^{-1}				
	1842	1741	1302	1162.5	791.
Bruckmann and Willner (1983[a])	12.4	32.6[c]	13.6	15.8	13.4
Stephens (1964, 1969[b])	10.0	23.6[d]	11.2	14.3	10.1

[a] At 4 mbar; no diluent; resolution 1.2 cm^{-1}.

[b] At 7 mbar in N_2 diluent at 973 mb total pressure and 295 K; grating instrument.

[c] Q branch resolved (1.5 torr).

[d] Q branch not resolved (1.4 mbar).

TABLE 3-4. PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE

Physical state, @25°C	Colorless liquid
Chemical formula	H_2O_2
Molecular weight	34.01
Melting point, °C	-0.41
Boiling point, °C, @760 mm Hg	150.2
Density, @25°C, 760 mm Hg	1.4422
Vapor pressure, @16.3°C	~1 mm Hg
Conversion factors @0°C, 760 mm Hg	1 ppm = 1520 $\mu g/m^3$; 1 $\mu g/m^3$ = 6.594×10^{-4} ppm
@25°C, 760 mm Hg	1 ppm = 1390 $\mu g/m^3$; 1 $\mu g/m^3$ = 7.195×10^{-4} ppm

Source: Weast (1977).

been reported to be a positive interference in measurements of total oxidants made by the Mast meter but to give a very slow response (slow color development) in the NBKI method for total oxidants (Chapter 4). This difference should be borne in mind when effects attributed to oxidants, as opposed to ozone, are evaluated. Second, H_2O_2 occurs normally as a substrate in biological systems and is involved in several redox pairs of biological importance (see, for example, West et al., 1966). It should also be noted that enzymes are present, at least in mammalian systems, that catalyze the breakdown of H_2O_2.

3.2.1.4 Formic Acid. Formic acid is a stable product formed in photochemical air pollution from, for example, the reaction of HO_2 radicals with HCHO and from the reactions of the Criegee biradical $\dot{C}H_2O\dot{O}$ with water vapor (Atkinson and Lloyd, 1984). It has been detected in polluted ambient atmospheres by longpath infrared spectroscopy on the basis of its characteristic Q-branch absorption at 1105 cm^{-1} (Hanst et al., 1975; Tuazon et al., 1978a, 1980, 1981a).

Formic acid has the structure of both an acid and an aldehyde and hence it differs in chemical behavior from other carboxylic acids in which the carboxyl group is linked to a hydrocarbon residue rather than to a lone hydrogen atom. In concentrated form, HCOOH is a pungent-smelling, highly corrosive liquid with a boiling point of 100.5°C.

3.2.2 Organic Precursors

This section briefly describes and defines those hydrocarbons and other volatile organic compounds commonly found in the ambient air of the United States and provides relevant information about their chemical and physical properties.

The term "hydrocarbon" has been used since the initial investigations of tropospheric photochemistry to represent those compounds of carbon and hydrogen that exist as gases in the ambient air and that participate along with oxides of nitrogen in reactions that form ozone and other photochemical oxidants. As knowledge of atmospheric chemistry has increased, some carbon compounds containing elements such as oxygen and the halogens have also been shown to be important in photochemical air pollution. Thus, the term "volatile organic compounds" (VOC) has come to be used to describe stable organic compounds that exist as gases under normal atmospheric conditions, most of which can participate in the formation of photochemical oxidants. Recognition that methane (CH_4) is virtually unreactive in the photochemical formation of ozone and other oxidants has given rise to the more accurate term, "nonmethane organic compounds" (NMOC), for describing those gas-phase organic compounds in ambient air that serve as precursors to ozone and other photochemical oxidants. While these three terms may sometimes appear to be used interchangeably in this chapter, the terminology used reflects that reported in the specific literature cited in this chapter, though in some instances differentiations may have been made for purposes of discussion.

As discussed in Chapter 4, methods for measuring total gas-phase hydrocarbons are not specific for hydrocarbons but may also detect other gas-phase organic compounds, though they will not measure them quantitatively. Where methods are used that permit speciation of the compounds measured, organic compounds other than hydrocarbons can be and usually are excluded from the summation of individual species used to arrive at a total nonmethane hydrocarbon (TNMHC) concentration. Where researchers have used methods that do not permit speciation, an indefinite and variable fraction of the reported TNMHC concentration may, in fact, be the result of the presence of nonhydrocarbon organics and such concentration data are more properly reported as total nonmethane organic compounds (NMOC).

The discussion that follows is aimed at presenting basic facts on nomenclature and those characteristics of photochemically reactive volatile organic compounds that are relevant to the information given subsequently in this and later chapters.

3.2.2.1 Hydrocarbons. Hydrocarbons are compounds consisting of hydrogen and carbon only. For a given homologous series the volatilities of hydrocarbons are related generally to the number of carbon atoms in each molecule, as well as to temperature. Hydrocarbons with a carbon number of one to four are gaseous at ordinary temperatures, while those with a carbon number of five or more are liquid or solid in pure state. Liquid mixtures of hydrocarbons such as gasoline may include some compounds in pure form that are gases, as well as those that are liquids. Likewise, gas-phase mixtures in ambient air will usually include compounds that are liquid or solid in their pure form. Hydrocarbons with a carbon number of about eight or less are abundant in ambient air, but those with a carbon number greater than about 12 have generally not been reported in the gas phase at significant concentrations, probably because of the inability of analytical techniques to detect these high molecular weight organics.

A saturated hydrocarbon has each of its carbon atoms bonded to four other atoms; whereas an unsaturated hydrocarbon has two or more carbon atoms bonded to fewer than four other atoms.

Alkanes. Alkanes, also known as paraffins, are saturated hydrocarbons having the general formula C_nH_{2n+2}. The first compound in the series is methane, CH_4, which, because of its low reactivity, does not contribute significantly to photochemical air pollution in urban atmospheres. Alkanes as a class are the least reactive of the photochemically important hydrocarbons (U. S. Environmental Protection Agency, 1978a,b). Alkanes may be straight- or branched-chain compounds, and comprise the open-chain (acyclic) hydrocarbons known as aliphatic hydrocarbons.

Alkenes. Alkenes, also known as olefins, have at least one unsaturated bond. The number of hydrogen atoms in the general formula of alkenes is decreased by two with respect to the alkanes for each double bond between carbon atoms; the general formula for alkenes with one double bond, for example, is C_nH_{2n}. The first compound in the alkene class is ethene, also known as ethylene; the second is propene, also known as propylene. For alkenes containing more than three carbon atoms the position of the double bond is specified by a numerical prefix (e.g., 1-butene). Compounds with carbon numbers three or higher can have two double bonds between the carbon atoms and are called dienes. The complete name of a diene is formed by including a prefix with numbers that indicate the location of the double bonds. Like alkanes, alkenes are aliphatic hydrocarbons and may exist as straight or branched chains. As a class, alkenes are among the most reactive hydrocarbons in photochemical systems (see Section 3.2.2.4).

Terpenes. Terpenes are a naturally occurring subgroup of alkenes, many of which have the formula $C_{10}H_{16}$. Among the terpenes identified in ambient air α- and β-pinene have been most frequently studied. Both α-

and β-pinene contain six-membered rings, as do several other terpenes; but at least one commonly occurring member of this group, myrcene, is an acyclic or open-chain compound. Isoprene, also a naturally occurring alkene, is a hemiterpene having the formula C_5H_8.

Alkynes. Alkynes are open-chain hydrocarbons that contain one or more triple bonds. Acetylene, C_2H_2, is the simplest member of the class, which as a whole is often referred to as the acetylenes. The general formula for the acetylenes is C_nH_{2n-2}, and for each additional triple bond in the molecule four hydrogen atoms must be removed from the general formula. Acetylene is commonly present in ambient air, is thought to be emitted largely from mobile sources, and has often been taken to be an indicator of auto exhaust emissions, since it is relatively unreactive in ambient air and persists in the atmosphere longer than most other exhaust components.

Aromatics. Aromatic hydrocarbons include various compounds having atoms arranged in six-membered carbon rings with only one additional atom (of hydrogen or carbon) attached to each atom in the ring. Benzene is the simplest compound in the series, having no side chains but only six carbon atoms and six hydrogen atoms, linked by three conjugated double bonds.

Compounds containing the aromatic ring and elements other than carbon and hydrogen are included with aromatic hydrocarbons in the general classification "aromatics." The double bonds in aromatics are not nearly as chemically active as those in alkenes because of an effect called "resonance stabilization." As a class, aromatics exhibit a wide range of photochemical reactivity, with benzene having a low photochemical reactivity and 1,3,5-trimethylbenzene, for example, showing high reactivity.

3.2.2.2 Aldehydes. Aldehydes probably constitute the single most abundant group of volatile organic compounds other than hydrocarbons in ambient air. They are photochemically important compounds because they photolyze to form free radicals that will react with oxygen in ambient air to form alkylperoxy or hydroperoxy radicals (National Research Council, 1977a) (see below).

Aldehydes are characterized by the presence of the formyl functional group (CHO). A carbonyl group having a carbon-oxygen double bond, C=0, is part of the formyl group. The carbonyl group is not unique to aldehydes, since it is found also in ketones and carboxylic acids; but it forms the basis for one of the analytical methods used for measuring aldehydes in ambient air (Chapter 4).

3.2.2.3 Other Organic Compounds. Other organic compounds found in ambient air are known to be photochemically reactive in the formation of ozone and other photochemical oxidants. These other organic compounds do not occur in ambient air collectively, much less singly, at concentrations that approach the total concentrations of nonmethane hydrocarbons. Some of them are suspected of having potentially adverse health effects, however, and are therefore under scrutiny by the U. S. Environmental Protection Agency. These compounds are mentioned here only because they are photochemically reactive, can serve as precursors to oxidants, and because they contribute a small but indeterminate fraction of the total NMOC concentrations reported when continuous hydrocarbon analyzers (Chapter 4) are used to determine ambient levels of volatile organic compounds.

Many of the volatile organics in ambient air that are not hydrocarbons are organic halides, in which one or more hydrogen atoms of a hydrocarbon have been replaced by a halogen atom such as chlorine, fluorine, or iodine. An enormous number of relatively simple organic halides are possible, since a halogen atom can be attached to an organic compound in many different positions.

3.2.2.4 Volatility and Reactivity. The physical and chemical properties of nonmethane organic compounds that are most pertinent to their role as precursors to ozone and other oxidants are those properties that govern their emission into the atmosphere (volatility) and their lifetime in the atmosphere, the latter being determined by photochemical reactions (reactivity) and other removal processes (e.g., gas-to-particle conversion and dry deposition).

To be significant in atmospheric reactions, an organic compound must have a sufficiently high volatility. Based upon a review of the available literature, Singh et al. (1984) have chosen a vapor pressure of 10^{-8} atm as the criteria for deciding whether an organic compound should be described as volatile. Those compounds with vapor pressures less than 10^{-8} atm were considered by Singh et al. (1984) to occur predominately in the condensed phase and therefore not to participate in atmospheric reactions. Clearly, a rigid cutoff for vapor pressures will not necessarily be applicable to all organic compounds.

The photochemical reactivity of subclasses and individual species of hydrocarbons and of other volatile organic compounds is relevant to mechanistic studies in atmospheric chemistry, to modeling, and to other oxidant-control-related research; but it is not pertinent to the derivation of criteria. A major discussion of these properties therefore lies outside the scope of this document, but a brief discussion of the concept of hydrocarbon reactivity and its application is presented here.

Differences in reactivities among volatile organic compounds have been the focus of considerable attention and research for nearly three decades. In early research on photochemical air pollution, many different definitions or criteria were used to evaluate the reactivity of organic compounds. Examples of such criteria include: rate of NO-to-NO_2 conversion, maximum ozone concentration formed, initial rate of disappearance of the organic compound, eye irritation, damage to vegetation, and aerosol formation.

Historically, reactivity classifications have been based on environmental chamber measurements of these criteria, as observed in the photooxidation of hydrocarbon-oxides of nitrogen mixtures under conditions approximating those of polluted ambient atmospheres. Many of the reactivity data that had been accumulated through 1969 for each of these manifestations (except plant damage) were critically reviewed by Altshuller and Bufalini in 1971. They noted general agreement in reactivity trends from studies employing different reactivity criteria, but they also cited a number of significant discrepancies in the specific assignments of reactivity to individual compounds and even to whole classes of compounds.

In recent years assessments of the reactivity of volatile organic compounds have focused almost exclusively on the ability of an organic compound to produce ozone and other photochemical oxidants. This focus arises from interest in regulating most stringently the emissions of organic compounds having the highest potential for forming ozone and other photochemical oxidants.

The 1978 criteria document for ozone and other photochemical oxidants summarized reactivity data acquired from the mid-1960s to the mid-1970s (U. S. Environmental Protection Agency, 1978a). Reference to tables of reactivity schemes given in the 1978 document shows the relatively higher reactivities of internally double-bonded alkenes, of aliphatic aldehydes and other carbonyl compounds (such as branched alkylketones and unsaturated ketones), of dienes, of 1-alkenes, of partially halogenated alkenes, and of alkylbenzenes (primary and secondary monoalkylbenzenes, and di-, tri- and tetraalkylbenzenes). Other compounds also have relatively high reactivity but are not expected to be as abundant in ambient air as the compounds cited above.

For more information the reader is referred to the 1978 criteria document (U. S. Environmental Protection Agency, 1978a) and the references therein [e.g., Dimitriades (1974) and Pitts et al. (1977)] for further information on reactivities of specific compounds. The reader is also referred to a more recent and comprehensive assessment of the present literature on the reactivity and volatility of 118 organic chemicals by Singh et al. (1984) in which a three-tiered classification scheme was developed based on the potential for involvement of a given chemical in photochemical air pollution formation.

Since a key reaction of volatile organic compounds in ambient air, regardless of their class, is their oxidation via attack by hydroxyl radicals (Atkinson et al., 1979, 1982c; Atkinson, 1985), the basis of several proposed reactivity classifications is the rate of reaction between an organic compound and the OH radical. This reaction is the first step in a chain reaction that is propagated by various organic peroxy radicals. As discussed in section 3.3.2.1, reaction with the OH radical is thought to be the predominant loss process for most organics in the troposphere (Atkinson et al., 1979; Atkinson, 1985). On this basis, a five-class reactivity scale was proposed by Pitts and coworkers (Darnall et al., 1976; Pitts et al., 1977) based on the rate of reaction of more than 100 VOC with OH radicals. In this scale, each class spanned an order of magnitude in reactivity relative to methane, with Class I corresponding to an atmospheric half-life of greater than 10 days and Class V a half-life of less than 2.5 hours. The scale has the advantage that any compound whose OH rate constant has been measured can be placed in a precise position in the scale. It has a number of limitations (Pitts et al., 1977), however, since it makes the implicit assumption that OH radical reaction is the sole loss process for an organic, and that the subsequent atmospheric chemistry is identical for all organic compounds. Both these limitations and the advantages of the OH radical reactivity scale are discussed in detail elsewhere (Pitts et al., 1977, 1985).

3.2.3 Nitrogen Oxides

The physical and chemical properties of the nitrogen oxides that serve as precursors in the formation of ozone and other photochemical oxidants have been documented in a recent air quality criteria document (U. S. Environmental Protection Agency, 1982a). The most pertinent properties are briefly summarized here. The role of nitrogen oxides in the formation of oxidants in the troposphere is discussed in Section 3.3 and in the document cited above.

The three most abundant oxides of nitrogen in ambient air are nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). The latter, a product of soil microbiology, is not known to participate in photochemical reactions in the troposphere. The two important oxides of nitrogen relative to photochemical processes in the troposphere are NO and NO_2, which are abundant in ambient air and participate in cyclic reactions leading to the production of ozone and other oxidants, as described later in this chapter.

The basic reactions of importance are (1) the photolysis of NO_2 ($\lambda <$ 430 nm); (2) subsequent formation of ozone from the reaction of atomic oxygen [$O(^3P)$] produced from the photolysis of NO_2 with O_2 (in the presence of a third, energy-absorbing molecule); and (3) the subsequent regeneration of NO_2 by the reaction of NO with O_3. Coupled with these basic reactions are reactions between NO and free radicals in the atmosphere (hydroperoxy, alkylperoxy and acylperoxy) that oxidize NO to NO_2, disturbing the NO-NO_2 equilibrium that would otherwise exist, and leading, then, to the buildup of O_3. These reactions, and further information on the source of the free radicals, are given below. Basic physical and chemical properties of NO and NO_2 are given in Table 3-5.

TABLE 3-5. PHYSICAL AND CHEMICAL PROPERTIES OF NITRIC OXIDE AND NITROGEN DIOXIDE

Property	NO	NO_2
Odor	None	Pungent
Taste	-	-
Color	None	Reddish-brown
Absorption λ, nm[a]	<230	Broad range, both >400 and <400
Other properties of note:	Uneven number of valence electrons	Corrosive, strong oxidant. Photolyzes at $\lambda < 430$ nm. Low partial pressure in ambient air. Uneven number of valence electrons. Forms dimers (N_2O_4).

[a] Visible light $\lambda > 400$ nm; ultraviolet $\lambda < 400$ nm. Solar UV radiation in the troposphere extends from about λ290 nm to about λ400 nm.

Source: Derived from National Research Council (1977b) and U. S. Environmental Protection Agency (1982a).

3.3 ATMOSPHERIC CHEMICAL PROCESSES: FORMATION AND TRANSFORMATION OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

> The photochemistry of the polluted atmosphere is exceedingly complex. Even if one considers only a single hydrocarbon pollutant, with typical concentrations of nitrogen oxides, carbon monoxide, water vapor, and other trace components of air, several hundred chemical reactions are involved in a realistic assessment of the chemical evolution of such a system. The actual urban atmosphere contains not just one but hundreds of different hydrocarbons, each with its own reactivity and oxidation products.
>
> (National Research Council, 1977a)

Despite the complexities of the chemistry of polluted atmospheres, it is sufficient to understand certain basic processes involved in the formation of photochemical oxidants from precursor compounds in the presence of sunlight. The concentrations of ozone and other oxidants found in urban areas and in downwind and rural receptor regions are the net result of at least three general processes: (1) the initial emission, dispersion, and transport of precursors; (2) the photochemical reactions that occur in the atmosphere as the dispersion and transport take place; and (3) the scavenging processes along the trajectory that reduce the concentrations both of precursors and the resulting oxidants.

Ozone (O_3) is formed in ambient air through the addition of an atom of oxygen (O) to a molecule of oxygen (O_2). The breakdown by sunlight (photolysis) of nitrogen dioxide (NO_2) into nitric oxide (NO) and atomic oxygen provide the atoms of oxygen involved. The NO formed in this reaction then reacts with the O_3 produced from the reaction between atomic and molecular oxygen. In these cyclic reactions, no net increase in O_3 occurs, with the result that an equilibrium is set up among O_3, NO_2, and NO. Any reactions that produce NO_2 without destroying O_3 will upset this equilibrium, however, and will result in a net increase in O_3. In ambient air, the oxidation of photochemically reactive hydrocarbons and other nonmethane organic compounds (NMOC) provides a source of reactive species (radicals) that convert NO to NO_2 without destroying O_3, thus upsetting the equilibrium. The reactions of these radicals with NO also constitute a cyclic process. Since terminating reactions occur between NO_2 and these radicals, as well, which remove both NO_2 and the radicals from the photochemical reaction system, the cycles described above would gradually end, even in the presence of sunlight, unless fresh NO_x emissions were injected into the atmosphere. The complexity of these cyclic, coupled reactions is such that ozone concentrations in ambient air are a nonlinear function of the NMOC and NO_x concentrations and, within realistic ranges of precursor concentrations, of the NMOC:NO_x ratio.

In the following sections, the processes just described in a simplistic and summary manner are presented in more detail. For a complete and thorough discussion of the many complex reactions thought to take place in polluted atmospheres, the primary literature should be consulted (e.g., Demerjian et al., 1974; Finlayson and Pitts, 1976; Logan et al., 1981; Whitten, 1983; Atkinson and Lloyd, 1984; and Atkinson, 1985).

3.3.1 Inorganic Reactions

3.3.1.1 Formation of Ozone: The NO-NO_2-O_3 Cycle. Many aspects of the inorganic reaction systems in the atmosphere are now well understood. The photodissociation of NO_2 by near-ultraviolet solar radiation is a critical process:

$$NO_2 + h\nu\ (295 \leq \lambda < 430\ \text{nm}) \rightarrow NO + O(^3P) \qquad (3\text{-}1)$$

The subsequent reaction of the resulting $O(^3P)$ atom with molecular oxygen produces an ozone molecule:

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (3\text{-}2)$$

where M is a "third body" molecule (e.g., N_2) which can carry away excess energy of reaction. In the absence of any competing reactions, the rapid reaction of NO with O_3 completes this reaction cycle, regenerating an NO_2 molecule:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3\text{-}3)$$

As a result of the above three reactions, an equilibrium or steady-state condition is established among NO, NO_2 and O_3, and the concentration of O_3 in the atmosphere is governed by the expression,

$$[O_3] = K \frac{[NO_2]}{[NO]} \qquad (3\text{-}4)$$

where $K = k_{3-1}/k_{3-3}$ which depends on the sunlight intensity. Typically, K in the lower troposphere is less than or equal to 0.025 ppm.

Because reaction (3-3) is rapid, ozone concentrations in urban atmospheres cannot rise until most of the NO has been converted to NO_2. This accounts in part for the fact that O_3 levels may be lower on average in city centers where high NO emissions occur, but higher in downwind suburban areas to which the resulting NO_2 is transported and then photodissociated, leading to O_3 formation. The characteristic behavior of irradiated NMOC-NO_x systems in producing O_3 and other photochemical oxidants is shown in Figure 3-1, which depicts data obtained from an environmental chamber irradiation of a propene-NO-NO_2 mixture (Pitts et al., 1979).

3.3.1.2 Formation of Radical Intermediates. Reactions (3-1) through (3-3), however, cannot by themselves explain the buildup of ozone, since for each molecule of NO oxidized to NO_2 in reaction (3-3) a molecule of ozone is also destroyed. An alternate pathway of conversion of NO to NO_2 that does not destroy O_3 is needed to explain the high ozone levels observed in urban environments. Such an alternate pathway is available through the oxidation of reactive organic compounds. In the atmosphere, these compounds can be oxidized by ozone (O_3) and/or hydroxyl radicals (OH).

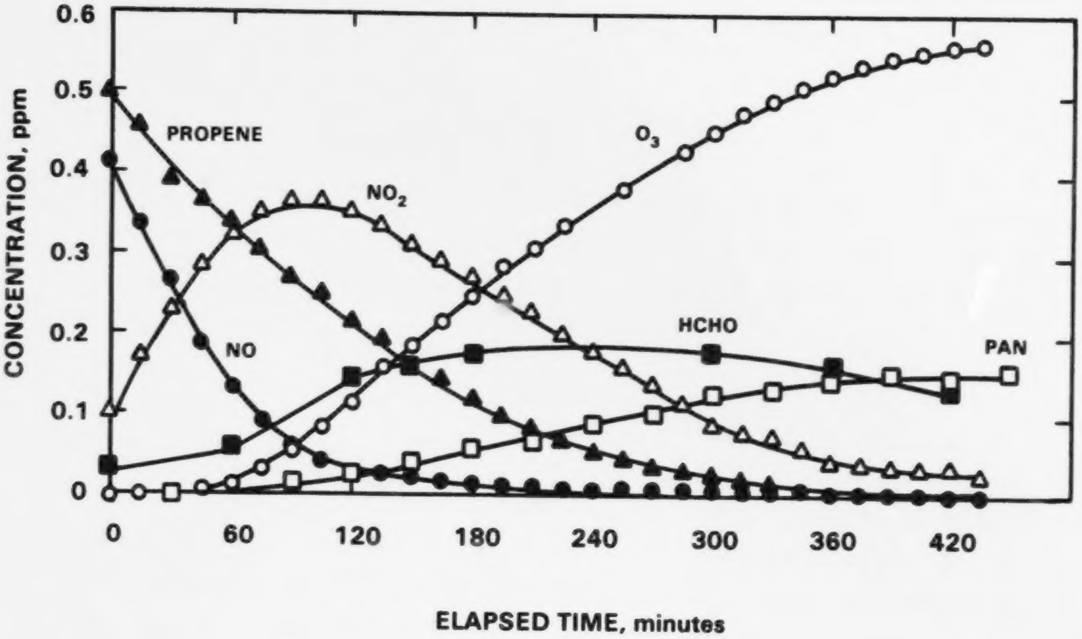


Figure 3-1. Experimental time-concentration profiles for propene, NO, NO_2, O_3, HCHO, and PAN for an irradiated NO_x-propene-air mixture.

Source: Pitts et al. (1979).

3.3.1.2.1 Hydroxyl and Hydroperoxyl Radicals. There are at least three significant formation routes leading to the production of hydroxyl radicals in the atmosphere. A pathway for OH radical formation, which becomes important in the afternoon as ozone concentrations rise, is the photolysis of O_3:

$$O_3 + h\nu\ (\lambda<319\ \mathrm{nm}) \rightarrow O(^1D) + O_2(^1\Delta g) \qquad (3\text{-}5)$$

The electronically excited $O(^1D)$ atoms may be quenched to ground state $O(^3P)$ atoms or may react with water vapor to yield OH radicals with an approximately 20 percent efficiency at 298 K and 50 percent relative humidity:

$$O(^1D) + H_2O \rightarrow 2\ OH \qquad (3\text{-}6)$$

Nitrous acid, which has been shown to accumulate to concentrations of ~1 to 8 parts-per-billion (ppb) during the night in the Los Angeles basin (Platt et al., 1980a; Harris et al., 1982; Pitts et al., 1984c) will photolyze at sunrise, producing a "pulse" of OH radicals (Harris et al., 1982):

$$HONO + h\nu\ (\lambda<400\ \mathrm{nm}) \rightarrow OH + NO \qquad (3\text{-}7)$$

This photolytic reaction represents a major sink for HONO during daylight hours. (Other aspects of the formation and atmospheric chemistry of this important species are discussed in Section 3.3.1.4.)

A third significant source of OH radicals is the photolysis of HCHO:

$$HCHO + h\nu\ (\lambda<370\ \mathrm{nm}) \begin{cases} \rightarrow H + HCO & (3\text{-}8a) \\ \rightarrow H_2 + CO & (3\text{-}8b) \end{cases}$$

Formaldehyde is both a primary (e.g., from motor vehicle exhausts) and secondary pollutant that may occur in significant concentrations in the morning hours as well as in the afternoon (Tuazon et al., 1978a, 1981a; Grosjean, 1982).

The H atoms formed in reaction (3-8a) or from reactions such as (3-9):

$$OH + CO \rightarrow CO_2 + H \tag{3-9}$$

can react with oxygen to produce hydroperoxyl radicals:

$$H + O_2 \xrightarrow{M} HO_2 + M \tag{3-10}$$

These can then react with NO to form hydroxyl radicals:

$$HO_2 + NO \rightarrow OH + NO_2 \tag{3-11}$$

Reaction (3-11) then completes a chain reaction involving reactions (3-9), (3-10) and (3-11) and is a major pathway for the oxidation of nitric oxide in ambient air.

The formyl radical in reaction (3-8a) may also serve as a precursor to HO_2 radicals and hence OH radical formation:

$$HCO + O_2 \rightarrow HO_2 + CO \tag{3-12}$$

Other sources of formyl radicals include the photolysis of higher aldehydes:

$$RCHO + h\nu\ (\lambda<350\ nm) \rightarrow R + HCO \tag{3-13}$$

In addition to reactions (3-11) and (3-12), HO_2 radicals are produced by H-atom abstraction from alkoxy radicals as discussed below:

$$RCH_2O + O_2 \rightarrow RCHO + HO_2 \tag{3-14}$$

These HO_2 radicals will also oxidize NO to NO_2 via reaction (3-11).

Based upon environmental chamber data, computer modeling studies and measured ambient concentrations of unreactive organics such as fluorochlorocarbons, concentrations of OH and HO_2 radicals in polluted atmospheres are believed to be in the ranges 5×10^5 to 5×10^6 and 10^8 to 10^9 radicals cm^{-3}, respectively.

3.3.1.2.2 Nitrate Radicals. Ozone can react with NO_2 to produce the nitrate radical and an oxygen molecule:

$$O_3 + NO_2 \rightarrow NO_3 + O_2; \qquad (3\text{-}15)$$

however, because of its large photolytic cross section (Graham and Johnston, 1978; Magnotta and Johnston, 1980) the NO_3 radical photolyzes rapidly in sunlight:

$$NO_3 + h\nu \rightarrow NO_2 + O(^3P) \qquad (3\text{-}16a)$$

$$\rightarrow NO + O_2 \qquad (3\text{-}16b)$$

Direct spectroscopic measurements (Platt et al., 1980b, 1984; Noxon. et al., 1980; Pitts et al., 1984c) have confirmed that NO_3 radical concentrations only rise above part-per-trillion (ppt) levels after sunset. The atmospheric reactions of this important radical intermediate are discussed in Sections 3.3.1.5 and 3.3.2.3, including the fact that at night the NO_3 radical will participate in a rapid equilibrium between NO_2, NO_3 and dinitrogen pentoxide (N_2O_5).

3.3.1.3 Termination Reactions. Although the photochemical reactions described above require sunlight, the presence of sunlight does not mean that the reactions continue indefinitely. Terminating reactions gradually remove NO and NO_2 from the reaction mixtures such that the cycles would slowly come to an end unless fresh NO_x emissions were injected into the atmosphere. Specifically, the inorganic chemistry system includes termination reactions for OH and HO_2 radicals with NO and NO_2 to form nitrogen acids such as nitrous acid (HONO), nitric acid (HNO_3) and peroxynitric acid (HO_2NO_2):

$$OH + NO \xrightarrow{M} HONO \qquad (3\text{-}17)$$

$$OH + NO_2 \xrightarrow{M} HNO_3 \qquad (3\text{-}18)$$

$$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2 \qquad (3\text{-}19)$$

Pernitric acid, however, thermally back-dissociates rapidly ($\tau_{1/2}$ ~10 sec at 298 K) and HONO photolyzes, so that under typical atmospheric conditions $OH + NO_2$ is the major sink of NO_x.

Nitrous acid and nitric acid have now both been reliably measured in ambient air by longpath spectroscopic techniques and, in the case of nitric acid by other techniques as well. Peroxynitric acid has not yet been observed in the atmosphere, although it has been predicted to be present at fractional ppb concentrations and has been extensively studied in laboratory systems (Graham et al., 1977; Hanst and Gay, 1977; Howard, 1977; Niki et al., 1977; Graham et al., 1978).

In the presence of NO, radical-radical reactions are generally not of major importance in the atmosphere, because concentrations of the radicals are low. In the absence of NO, however (for example at night), the reactions of peroxy radicals with HO_2 and with other peroxy and acylperoxy radicals, and the self-combination of HO_2 radicals, can become important. For example, the reaction of HO_2:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (3\text{-}20)$$

could be an important route to the oxidation of SO_2 to sulfate in solution (see section 3.3.4).

Clearly, termination of the chain reactions can lead to the formation of other oxidants as well as relatively stable organic nitrates in the atmosphere. In addition to HONO, HNO_3, HO_2NO_2 and H_2O_2, these oxidants include other peroxyacyl nitrates, organic hydroperoxides and organic peracids which have been observed either in polluted atmospheres or in irradiated laboratory mixtures (National Research Council, 1977a). These compounds almost always occur in low concentrations in ambient air, but they may play a significant or even critical role in atmospheric chemistry (Pitts et al., 1983) as shown in the following sections.

3.3.1.4 Reactions Involving Nitrous Acid. An alternative pathway for reaction (3-19) is the formation of HONO:

$$HO_2 + NO_2 \rightarrow HONO + O_2 \qquad (3\text{-}21)$$

This reaction pathway has been shown, however (Graham et al., 1977, 1978; Howard, 1977), to be negligible compared to reaction (3-19).

The equilibrium between NO, NO_2, and H_2O results in still another potential source of HONO:

$$NO + NO_2 + H_2O \rightarrow 2\ HONO \qquad (3\text{-}22)$$

$$2\ HONO \rightarrow NO + NO_2 + H_2O \qquad (3\text{-}23)$$

Reactions (3-22) and (3-23) may proceed both homogeneously and heterogeneously, but they appear to be too slow to be of atmospheric importance at part-per-million concentrations of NO_x.

Similarly, the reaction of NO_2 with water may proceed in the gas phase or on surfaces:

$$2\ NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad (3\text{-}24)$$

Recent work (Sakamaki et al., 1983; Pitts et al., 1984a) has shown that HONO is produced in environmental chambers from the reaction of NO_2 with water vapor, almost certainly via heterogeneous processes (although HNO_3 was not observed in these studies). This process may be a minor source of HONO in the atmosphere and in the exhaust plumes from combustion sources (Pitts et al., 1984b).

3.3.1.5 Reactions Involving Nitric Acid and Dinitrogen Pentoxide.

Another equilibrium reaction of importance is that involving NO_2, NO_3, and N_2O_5:

$$NO_2 + NO_3 \overset{M}{\rightleftarrows} N_2O_5 \qquad (3\text{-}25a,b)$$

The equilibrium constant for this system has been measured by several groups (Graham and Johnston, 1978; Kircher et al., 1984; Tuazon et al., 1984; Perner et al., 1985) and appears to be 3 (±0.5) x 10^{-11} cm^3 $molecule^{-1}$ at 298 K, which corresponds to a time to reach equilibrium of about one minute. The equilibrium constant remains somewhat uncertain, however.

Dinitrogen pentoxide is a potentially important precursor to HNO_3 (and hence acid deposition) through its reaction with water either in the gas phase (Tuazon et al., 1983) or on surfaces (Heikes and Thompson, 1983):

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \qquad (3\text{-}26)$$

Thus, for NO_2 and NO_3 radical concentrations representative of receptor sites downwind from major urban areas such as Los Angeles (Pitts et al., 1983, 1984c; Platt et al., 1984), and using an $NO_2 + NO_3 \leftrightarrows N_2O_5$ equilibrium constant of 3×10^{-11} cm^3 $molecule^{-1}$, an HNO_3 formation rate of several ppb hr^{-1} is obtained at ~50 percent relative humidity [assuming the upper limit rate constant of 1.3×10^{-21} cm^3 $molecule^{-1}$ sec^{-1} for reaction (3-26)].

This estimated nighttime formation rate of HNO_3 via reaction (3-26) can be compared to a calculated daytime formation rate of ~1 ppb hr^{-1} from reaction (3-18) for ~20 ppb of NO_2 and 1×10^6 molecule cm^{-3} of OH radicals. Reaction (3-26) could potentially be an important loss process for NO_x and a significant nighttime pathway for HNO_3 formation in urban atmospheres.

3.3.2 Organic Reactions

It is now well recognized that all organic compounds emitted into the atmosphere may be degraded by one or more of the following four pathways: reaction with hydroxyl radicals, reaction with ozone, reaction with nitrate radicals, or photolysis. Indeed, knowledge of the rates and mechanisms of these processes has advanced to the point that the process that will predominate for a given compound can be predicted with a reasonable degree of certainty.

This progress notwithstanding, there remain substantial differences in the degree to which the detailed atmospheric chemistry is understood for the principal classes of hydrocarbons found in polluted atmospheres: alkanes (paraffins), alkenes (olefins), and aromatics. Thus, the photooxidation reactions of the smaller alkanes and the simple alkenes, such as ethene, propene, and *trans*-2-butene, are fairly well understood. There is much less certainty, however, about the detailed reactions undergone by the higher alkanes, the higher alkenes, and the aromatics subsequent to their initial reactions with OH radicals, ozone, or NO_3 radicals.

The following sections briefly summarize the basic features of the four reaction pathways identified above for organic compounds emitted into the atmosphere.

3.3.2.1 Reactions with Hydroxyl Radicals. The following sections treat separately the mechanisms of reaction of OH radicals with the major classes of organic compounds including alkanes, alkenes, aromatics and oxygenated compounds, as well as nitrogen- and sulfur-containing compounds. The treatment here of relevant reactions is necessarily an overview. For a comprehensive and current detailed description of the kinetics and mechanisms of the atmospheric reactions of OH radicals with organic compounds, the reader is referred to a review by Atkinson (1985).

3.3.2.1.1 Alkanes. It is now well established that the only significant atmospheric chemical loss process for the alkanes is reaction with OH radicals. These reactions proceed by hydrogen abstraction (Atkinson, 1985) to produce alkyl radicals (R), which then add O_2 to form alkyl peroxy radicals (RO_2):

$$OH + RH \rightarrow R^{\bullet} + H_2O \qquad (3\text{-}27)$$

$$R^{\bullet} + O_2 \xrightarrow{M} RO_2^{\bullet} \qquad (3\text{-}28)$$

In polluted atmospheres RO_2 radicals rapidly oxidize NO to NO_2, forming alkoxy radicals (RO); or add NO_2 to form alkyl peroxynitrates:

$$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \qquad (3\text{-}29)$$

$$RO_2^{\bullet} + NO_2 \rightleftarrows RO_2NO_2 \qquad (3\text{-}30a,b)$$

The latter, however, are not expected to be present in ambient air at significant concentrations because of their short ($\leq$1 sec at 298 K) lifetimes with respect to thermal decomposition (reaction 3-30b).

Alkoxy radicals may also undergo hydrogen abstraction by molecular oxygen to form aldehydes or ketones (Baldwin et al., 1977):

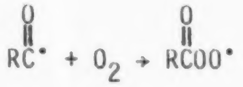
$$R'RCHO^{\bullet} + O_2 \rightarrow R'OR + HO_2^{\bullet} \qquad (3\text{-}31)$$

or they may decompose to form oxygenates (Baldwin et al., 1977; Batt, 1979):

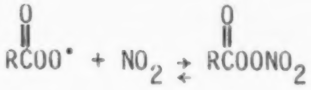
$$R'RCHO^{\bullet} \rightarrow \begin{cases} RCHO + R'^{\bullet} & (3\text{-}32) \\ R'CHO + R^{\bullet} & (3\text{-}33) \end{cases}$$

In both of these reaction sequences, however, HO_2 radicals are formed, and hence OH radicals are regenerated. The carbonyl compounds thus formed may subsequently react with OH radicals or may photodecompose (see Section 3.3.2.1.4).

A further important reaction pathway for acyl radicals is the addition of O_2, followed by reaction with NO_2 to form peroxyacyl nitrates:



$$R\overset{\overset{O}{\|}}{C}{}^{\cdot} + O_2 \rightarrow R\overset{\overset{O}{\|}}{C}OO^{\cdot} \tag{3-34}$$



$$R\overset{\overset{O}{\|}}{C}OO^{\cdot} + NO_2 \rightleftarrows R\overset{\overset{O}{\|}}{C}OONO_2 \tag{3-35}$$

The simplest member of this class of compounds, peroxyacetyl nitrate, has been measured in polluted atmospheres throughout the world (see Chapter 5).

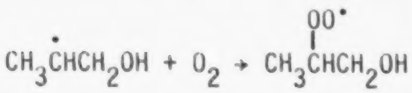
The reactions described above suggest the importance of simple ($\leq C_4$) alkoxy and alkylperoxy radicals in atmospheric chemistry. In addition to these reactions for the simple alkanes, two other processes involving $RO^{\cdot}$ and $RO_2^{\cdot}$ reactions occur for larger ($\geq C_4$) alkanes, namely alkoxy radical isomerization (Carter et al., 1976; Baldwin et al., 1977; Hendry et al., 1978; Batt, 1979; Batt and Robinson, 1979; Carter et al., 1979) and alkyl nitrate formation from the reaction of $RO_2^{\cdot}$ with NO (Atkinson et al., 1982a, 1983, 1984f):

$$RO_2^{\cdot} + NO \xrightarrow{M} RONO_2 \tag{3-36}$$

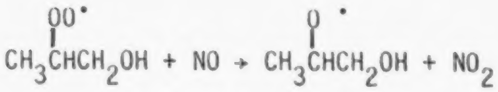
Discussion of these processes is beyond the scope of this chapter and the reader is referred to the original literature and to appropriate reviews (e.g., Atkinson, 1985) for summaries of these aspects of the atmospheric chemistry of longer-chain alkanes.

3.3.2.1.2 Alkenes. In polluted atmospheres, unsaturated hydrocarbons react primarily with OH radicals and with O_3 (Herron and Huie, 1977, 1978; Dodge and Arnts, 1979; Akimoto et al., 1980; Kan et al., 1981; Niki et al., 1981; Atkinson et al., 1982c; Whitten, 1983; Atkinson, 1985). For most alkenes studied to date, the reaction with OH radicals proceeds almost entirely by addition to the double bond. In the case of propene, for example, addition of the OH radical to the double bond is expected to be followed by O_2 addition, with the oxidation of NO to NO_2 by the resulting peroxy radical to form an alkoxy radical (Atkinson et al., 1985):

$$OH^{\bullet} + CH_3CH{=}CH_2 \rightarrow CH_3\dot{C}HCH_2OH \qquad (3\text{-}37)$$

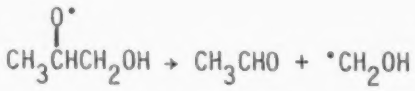


$$CH_3\dot{C}HCH_2OH + O_2 \rightarrow CH_3\overset{OO^{\bullet}}{\overset{|}{C}}HCH_2OH \qquad (3\text{-}38)$$

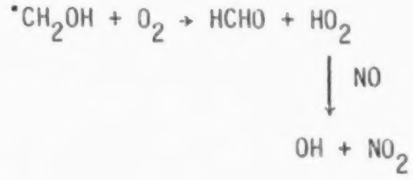


$$CH_3\overset{OO^{\bullet}}{\overset{|}{C}}HCH_2OH + NO \rightarrow CH_3\overset{O^{\bullet}}{\overset{|}{C}}HCH_2OH + NO_2 \qquad (3\text{-}39)$$

Decomposition of the alkoxy radical and subsequent reactions lead to the formation of acetaldehyde and formaldehyde, both of which can be detected in polluted atmospheres:

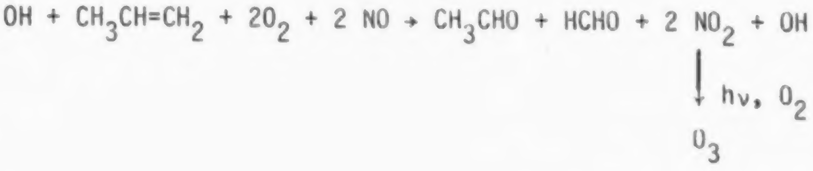


$$CH_3\overset{O^{\bullet}}{\overset{|}{C}}HCH_2OH \rightarrow CH_3CHO + {}^{\bullet}CH_2OH \qquad (3\text{-}40)$$



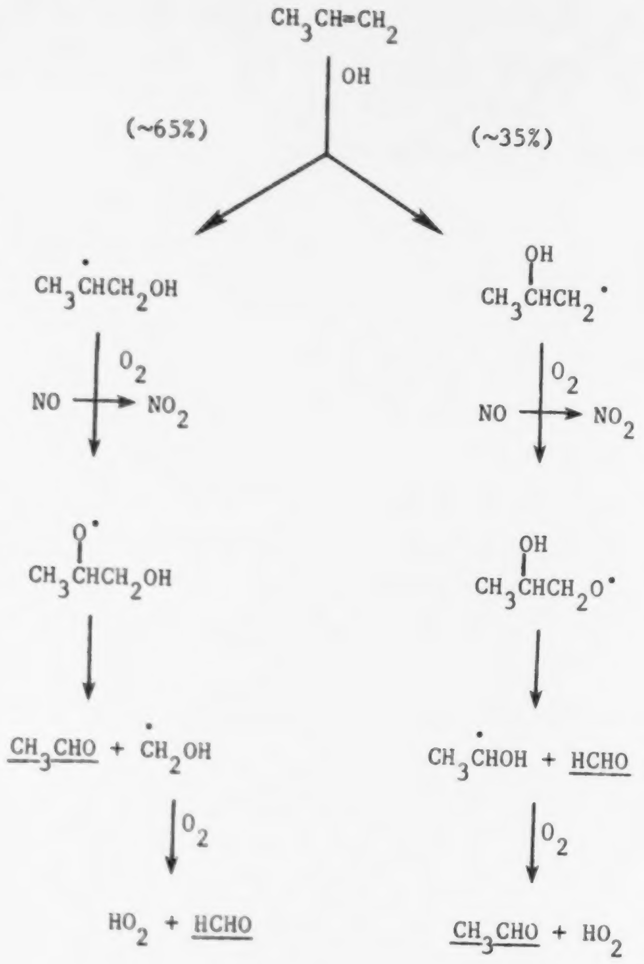
$$^{\bullet}CH_2OH + O_2 \rightarrow HCHO + \underset{OH\,+\,NO_2}{\underset{\downarrow\,NO}{HO_2}} \qquad (3\text{-}41)$$

The overall reaction resulting from reactions (3-37) to (3-41) is:



$$OH + CH_3CH{=}CH_2 + 2O_2 + 2\,NO \rightarrow CH_3CHO + HCHO + 2\,\underset{O_3}{\underset{\downarrow\,h\nu,\,O_2}{NO_2}} + OH \qquad (3\text{-}42)$$

Thus, the reaction of OH radicals with alkenes increases the rate of NO-to-NO_2 conversion and hence increases the yield of ozone. The specific reaction sequence for the OH radical-initiated oxidation of propene (Atkinson, 1985) is shown in Figure 3-2.



$CH_3CH{=}CH_2$
OH
(~65%)
(~35%)
$CH_3\dot{C}HCH_2OH$
$CH_3CH(OH)CH_2^{\bullet}$
O_2
NO
NO_2
$CH_3CH(O^{\bullet})CH_2OH$
$CH_3CH(OH)CH_2O^{\bullet}$
CH_3CHO + $\dot{C}H_2OH$
$CH_3\dot{C}HOH$ + HCHO
HO_2 + HCHO
CH_3CHO + HO_2

Figure 3-2. Reaction scheme for OH radical-initiated oxidation of propene in the presence of NO.

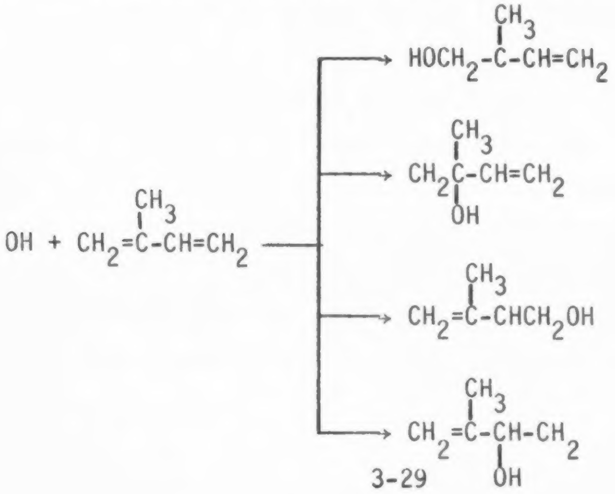
Source: Atkinson (1985).

The reaction schemes presented for propene illustrate the major role that organic compounds (not only alkenes but also alkanes and aromatics) play in producing photochemical air pollution, namely acceleration of the conversion of NO to NO_2 and the resulting formation of ozone.

Alkenes Emitted From Vegetation. A special class of alkenes receiving considerable attention over the past decade are those unsubstituted compounds emitted from vegetation. Examples include isoprene and monoterpenes such as α- and β-pinene, d-limonene, and myrcene. Much research and discussion have been devoted to assessments of the potential for such compounds, which are emitted from vegetation in large quantities, to contribute to photochemical air pollution (Coffey, 1977; Westberg, 1977; Arnts and Gay, 1979; Tingey and Burns, 1980; Bufalini and Arnts, 1981; Dimitriades, 1981; Altshuller, 1983), but a detailed treatment of this topic is beyond the scope of this document. Presented here, and in other appropriate parts of section 3.3, are relevant aspects of current knowledge of the atmospheric chemistry of organic compounds known to be emitted from vegetation.

Although reliable rate constants for the reaction of these naturally emitted organic compounds with OH radicals are now available (Winer et al., 1976; Kleindienst et al., 1982; Atkinson, 1985), with the exception of isoprene their detailed atmospheric chemistry is still not well characterized. Summarized briefly here are the OH radical-initiated photooxidation reactions for isoprene and α-pinene.

Isoprene. Based on the relative atmospheric concentrations of OH radicals and ozone, and their rate constants for reaction with isoprene, the dominant atmospheric reaction pathway for isoprene is expected to be OH radical addition to the olefinic double bonds (Lloyd et al., 1983):



$$\mathrm{OH} + \mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2} \longrightarrow \mathrm{HOCH_2{-}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2} \qquad (3\text{-}43a)$$

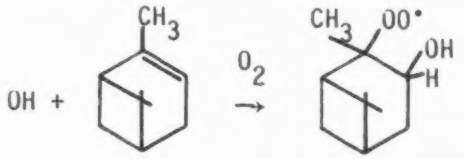
$$\longrightarrow \mathrm{CH_2\underset{\underset{OH}{|}}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH_2} \qquad (3\text{-}43b)$$

$$\longrightarrow \mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CHCH_2OH} \qquad (3\text{-}43c)$$

$$\longrightarrow \mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\underset{\underset{OH}{|}}{CH}{-}CH_2} \qquad (3\text{-}43d)$$

The hydroxyalkyl radicals formed in reactions (3-43a)-(3-43d) react rapidly with O_2 to form peroxy radicals, which can then rapidly oxidize NO to NO_2 (Atkinson and Lloyd, 1984). The resulting hydroxyalkoxy radicals decompose to form methyl vinyl ketone and methacrolein. The subsequent atmospheric reactions of these products are described in detail by Lloyd et al. (1983) and by Killus and Whitten (1984).

α-Pinene. Based on the rate constant for its reaction with OH radicals (Atkinson et al., 1979; Kleindienst et al., 1982), α-pinene is expected to react exclusively by OH radical addition at the least substituted carbon atoms, with the resulting radical rapidly adding O_2 (Lloyd et al., 1983):



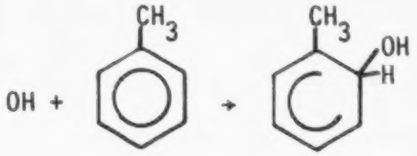
(3-44)

A mechanism for the subsequent reaction pathways of this hydroxyperoxy radical has been reported (Lloyd et al., 1983), but it was of necessity largely parameterized because of the lack of data on the reaction products resulting from the photooxidation of α-pinene under atmospheric conditions. Even less information is available for other monoterpenes and any detailed consideration of their atmospheric chemistry would be highly speculative.

For further descriptions of the OH radical-initiated photooxidations of isoprene and monoterpene, the reader should consult the primary literature (Lloyd et al., 1983; Killus and Whitten, 1984).

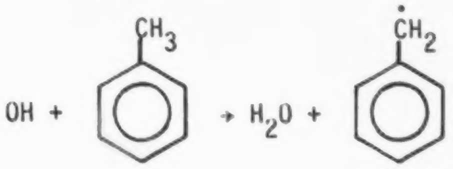
3.3.2.1.3 Aromatics. The aromatic fraction in gasolines has increased in recent years, partly as a result of the reduction of lead in gasoline. Given that there are also substantial emissions of aromatic compounds (e.g., benzene, toluene, xylenes, etc.) from a wide range of industrial processes, the importance of aromatics in the hydrocarbon distribution in ambient atmospheres has grown.

Reactions with OH radicals constitute the sole atmospheric loss process for aromatic compounds. The available kinetic and mechanistic data concerning these reactions have been reviewed critically (Atkinson, 1985). It is clear from these data that two reaction pathways are possible. The first of these is OH radical addition to the aromatic ring to form an initially energy-rich OH-aromatic adduct which can either decompose back to the reactants or be collisionally stabilized. This is illustrated for toluene, an abundant aromatic constituent in urban atmospheres:



(plus other isomers) (3-45)

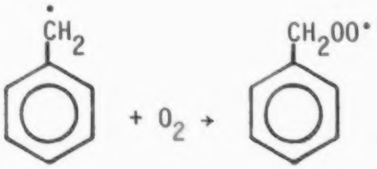
For alkyl-substituted benzenes, the second reaction pathway involves H-atom abstraction from the substituent group:



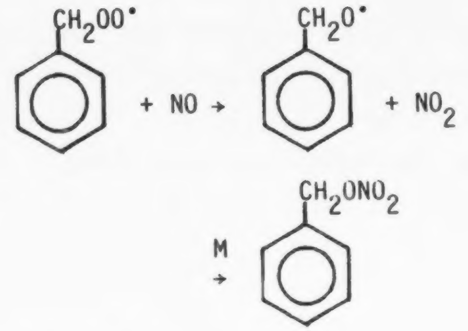
(A)

(3-46)

This latter is a minor ($\lesssim$10%) process at room temperature (Atkinson, 1985). The reaction pathways subsequent to the H-atom abstraction reaction pathway (3-46) are reasonably well understood (Atkinson and Lloyd, 1984). Thus, under atmospheric conditions the benzyl radical is expected to react via the following sequence of reactions:



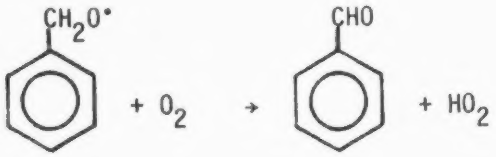
(3-47)



(3-48a)

(3-48b)

with reaction (3-48b) occurring approximately 10 percent of the time at atmospheric pressure and room temperature (Hoshino et al., 1978). The $C_6H_5CH_2O^\bullet$ radical then reacts with O_2 to yield benzaldehyde and an HO_2 radical:



(3-49)

Analogous reaction pathways are expected to be applicable to the other aromatic hydrocarbons, after H-atom abstraction from the substituent alkyl groups (Atkinson and Lloyd, 1984).

The rates of reaction of OH radicals with aromatics are now well characterized (Atkinson, 1985), as is the relative importance of the alternative pathways (3-45) vs (3-46), at least for selected aromatics. In the case of toluene, for example, OH radical addition is expected to occur ~80 percent of the time at the ortho position (Kenley et al., 1981).

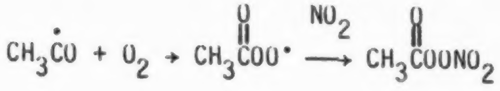
The fate, however, of the addition adducts formed from OH radical-aromatic reactions remains unclear (Atkinson, 1985), although several mechanisms have been proposed in the case of toluene (Atkinson et al., 1980; Leone et al., 1985). Although substantial progress has been made in understanding reaction mechanisms for toluene and certain other aromatic hydrocarbons (Atkinson and Lloyd, 1984; Leone et al., 1985), much additional research is needed before a complete understanding of the complex NO_x-photooxidation chemistry of aromatic compounds is obtained.

3.3.2.1.4 Aldehydes. Aldehydes are consumed in the atmosphere both by photolysis and attack by OH radicals. Photolysis of acetaldehyde, for example, leads to methyl and formyl radicals that then react as discussed above:

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \qquad (3\text{-}50)$$

Attack by OH radicals forms acetyl radicals which can successively add O_2 and NO_2 to form PAN:

$$CH_3CHO + OH \rightarrow CH_3\dot{C}O + H_2O \qquad (3\text{-}51)$$



$$CH_3\dot{C}O + O_2 \rightarrow CH_3\overset{O}{\overset{\|}{C}}OO^{\bullet} \xrightarrow{NO_2} CH_3\overset{O}{\overset{\|}{C}}OONO_2 \qquad (3\text{-}52)$$

3.3.2.1.5 Nitrogen-Containing Compounds. Only limited information is available for the reactions of OH radicals with nitrogen-containing compounds and their subsequent reactions under atmospheric conditions. The OH radical reactions with the aliphatic amines are rapid, with room temperature rate constants being in the range (2-6) x 10^{-11} cm^3 $molecule^{-1}$ sec^{-1} (Atkinson et al., 1985). For the methyl-substituted amines, the trend of the room temperature rate constants suggests that these reactions proceed via abstraction from the C-H bonds and, where possible, the N-H bonds. Product studies of several irradiated amine-air systems have been reported in which plausible reaction pathways following OH radical attack have been proposed (Pitts et al., 1978; Tuazon et al., 1978b; Lindley et al., 1979).

To date, kinetic data are available only for OH radical reactions with hydrazine and methylhydrazine (Atkinson, 1985), and only limited product data are available for these reactions (Tuazon et al., 1981b, 1982). Reactions of nitrites with OH radicals are expected to proceed via H-atom abstraction from the C-H bonds but, since no product data are presently available, no reliable assessment of the initial reaction pathway can be made.

No product or direct mechanistic data are available for organic nitrates. However, the reactions of OH radicals with at least the smaller alkyl nitrates (for which isomerization of the alkoxy radicals cannot occur) will probably ultimately yield NO_2 together with the corresponding aldehydes (Atkinson et al., 1982d). These reactions may be of importance in long-range transport and acid deposition, since alkyl nitrates are formed in significant yields from the atmospheric photooxidation of certain alkanes (Atkinson and Lloyd, 1984).

3.3.2.1.6 Sulfur-Containing Compounds. The literature concerning reactions of sulfur-containing compounds with OH radicals has been reviewed recently by Atkinson (1985). Reactions of thiols with OH radicals must proceed via either H-atom abstraction from the weak S-H bonds or, more likely, by the formation of an OH-thiol adduct. The reaction of OH radicals with the sulfides, RSR, can proceed via either H-atom abstraction from the C-H bonds or OH radical addition to the sulfur atom. Product data for the reaction of OH radicals with dimethyl sulfide under atmospheric conditions have been obtained from numerous studies (Grosjean and Lewis, 1982; Hatakeyama et al., 1982; Hatakeyama and Akimoto, 1983; Niki et al., 1983; Grosjean, 1984); the major stable products are HCHO, SO_2 and CH_3SO_3H, together with CH_3SNO as an intermediate product.

Only for dimethyl disulfide have kinetic (Cox and Sheppard, 1980; Wine et al., 1981) and product (Hatakeyama and Akimoto, 1983) data been reported. On the basis of these data, it appears that the initial reaction proceeds via OH radical addition to form an adduct, followed by rapid decomposition of this adduct to CH_3S and CH_3SOH radicals. Subsequent reactions of these CH_3SOH and CH_3S radicals then lead to the observed products: SO_2, HCHO, and CH_3SO_3H.

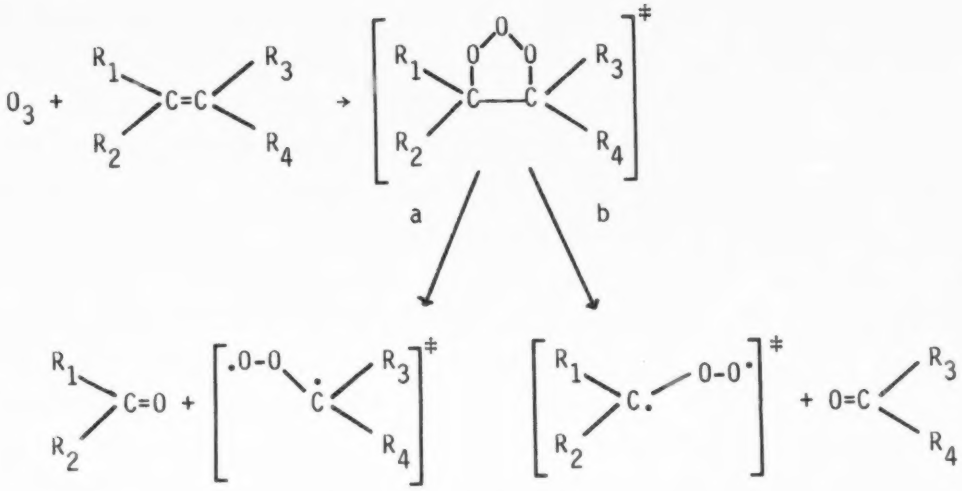
3.3.2.2 Reactions with Ozone. The atmospheric reactions of ozone are complex and result in products and processes that have significant environmental implications, including effects on biological systems, visibility, and materials. Ozone, for example, is highly reactive towards certain classes of organic compounds (e.g., alkenes) and certain of those reactions lead to the formation of secondary organic aerosols. Ozone may also play a role in the oxidation of SO_2 to H_2SO_4, both indirectly in the gas phase (via formation of OH radicals and Criegee biradicals) and directly in aqueous droplets.

In the following sections, the atmospheric reactions of ozone with organic compounds are summarized in some detail, including the mechanisms of certain of these reactions. Emphasis is placed, whenever possible, on those reactions that lead to products or processes suspected or known to have effects on biological or other important receptors.

In discussing the reactions of ozone with organic compounds in the troposphere, it is important to recognize that organics undergo competing reactions with OH radicals during daytime hours (Atkinson and Lloyd, 1984; Atkinson, 1985) and, in certain cases, they can photolyze or react with NO_3 radicals at night (Japar and Niki, 1975; Carter et al., 1981a; Atkinson et al., 1984a,b,c,d; Winer et al., 1984). All organics except the perhaloalkanes exhibit room temperature OH radical rate constants of $\gtrsim 5 \times 10^{-15}$ cm^3 $molecule^{-1}$ sec^{-1} (Atkinson, 1985). Since the ratio of O_3 to OH radical concentrations in the unpolluted troposphere during daylight hours is believed to be of the order of 10^6 (Singh et al., 1978; Crutzen, 1982), only for those organics whose O_3 reaction rate constants are greater than $\sim 10^{-21}$ cm^3 $molecule^{-1}$ sec^{-1} can consumption by O_3 be considered atmospherically important. These ozone reactions of interest are summarized below.

3.3.2.2.1 Alkenes. Ozone reacts rapidly with the acyclic mono-, di- and trialkenes and cyclic mono-, di-, and tri-alkenes. The rate constants for these reactions range from $\sim 10^{-18}$ to $\sim 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} (Atkinson and Carter, 1984), corresponding to atmospheric lifetimes ranging from a few minutes (for the more reactive cyclic alkenes such as the monoterpenes) to several days. In polluted atmospheres, especially in the afternoons during photochemical oxidant episodes, the principal consumption of the more reactive alkenes will therefore occur via reaction with O_3, rather than with OH radicals.

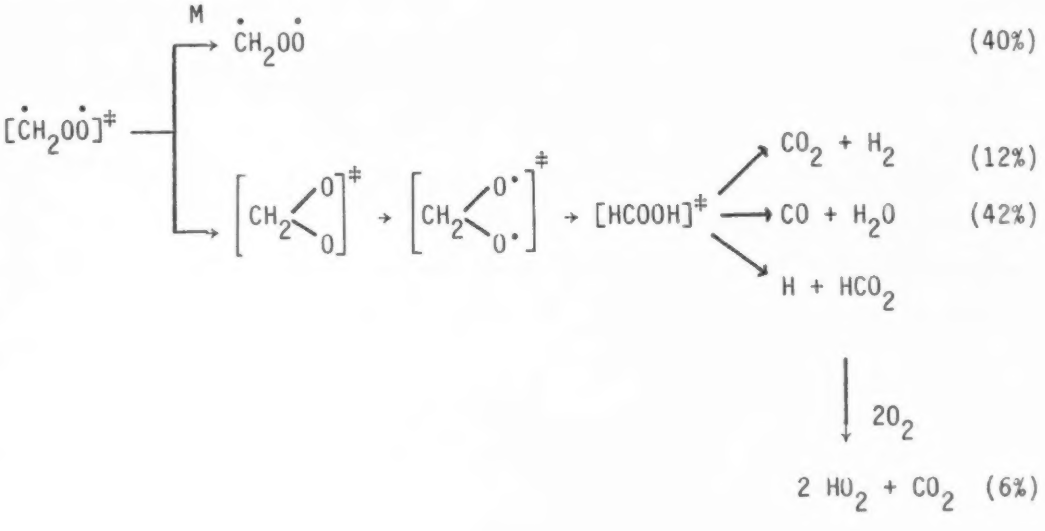
It is now reasonably well established that the initial step in the O_3-alkene reaction involves the formation of a "molozonide" that rapidly decomposes (Harding and Goddard, 1978; Herron et al., 1982) to a carbonyl compound and a biradical (which is also initially energy rich):


O_3 +
R_1
R_2
C=C
R_3
R_4
‡
a
b
.O-O
C=O +
O-O·
+ O=C

(3-53)

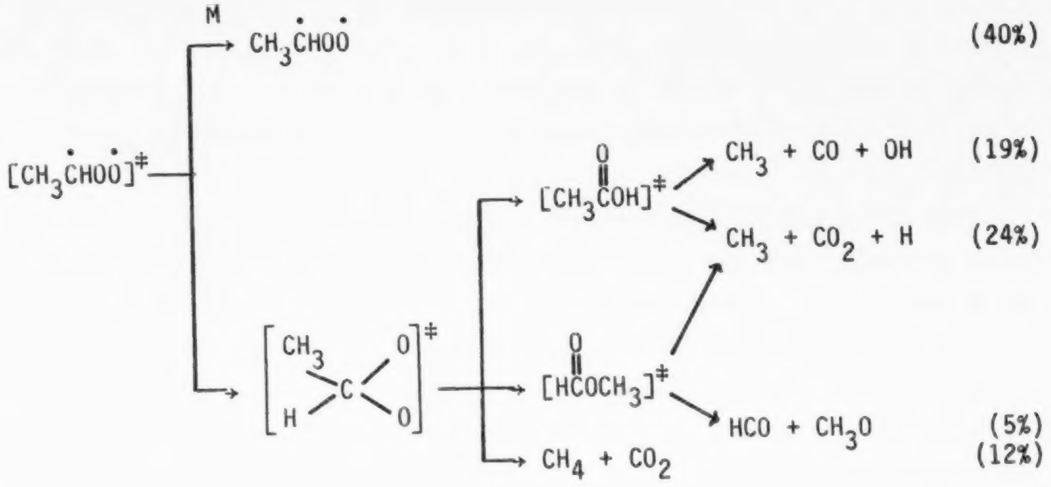
where [ ]‡ denotes an energy-rich species.

Based on an analysis of reported product and mechanistic studies of the reactions of O_3 with ethene (Herron and Huie, 1977; Su et al., 1980; Kan et al., 1981; Niki et al., 1981) and propene (Herron and Huie, 1978; Dodge and Arnts, 1979), and the much less extensive studies of the higher alkenes (Martinez et al., 1981), Atkinson and Lloyd (1984) have suggested that these initially energy-rich biradicals react under atmospheric conditions as shown below:


M
$\dot{C}H_2O\dot{O}$
(40%)
$[\dot{C}H_2O\dot{O}]^‡$
CH_2
[HCOOH]‡
$CO_2 + H_2$
(12%)
$CO + H_2O$
(42%)
$H + HCO_2$
$2O_2$
$2\ HO_2 + CO_2$
(6%)

(3-54)

and


M
$CH_3\dot{C}HO\dot{O}$
(40%)
$[CH_3\dot{C}HO\dot{O}]^{\ddagger}$
$[CH_3\overset{O}{\overset{\|}{C}}OH]^{\ddagger}$
$CH_3 + CO + OH$
(19%)
$CH_3 + CO_2 + H$
(24%)
CH_3
H
C
O
O
$[H\overset{O}{\overset{\|}{C}}OCH_3]^{\ddagger}$
$HCO + CH_3O$
(5%)
$CH_4 + CO_2$
(12%)

(3-55)

where $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ denote thermalized biradicals. These thermalized biradicals have been shown (Calvert et al., 1978; Herron et al., 1982; Atkinson and Lloyd, 1984) to undergo bimolecular reactions with aldehydes, SO_2, CO, and H_2O, and it is believed that they will also react with NO and NO_2 (Calvert et al., 1978; Herron et al., 1982; Atkinson and Lloyd, 1984):

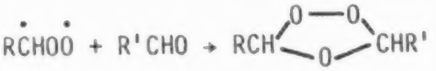
$$R\dot{C}HO\dot{O} + NO \rightarrow RCHO + NO_2 \qquad (3\text{-}56)$$

$$R\dot{C}HO\dot{O} + NO_2 \rightarrow RCHO + NO_3 \qquad (3\text{-}57)$$

$$R\dot{C}HO\dot{O} + SO_2 \xrightarrow{H_2O} RCHO + H_2SO_4 \qquad (3\text{-}58)$$

$$R\dot{C}HO\dot{O} + H_2O \rightarrow RCOOH + H_2O \qquad (3\text{-}59)$$

$$R\dot{C}HO\dot{O} + CO \rightarrow \text{products} \qquad (3\text{-}60)$$


$R\dot{C}HO\dot{O} + R'CHO \rightarrow$
RCH
O
O
O
CHR'

(3-61)

Under atmospheric conditions, the reactions with NO, NO_2, or H_2O are expected to be the dominant loss processes of these thermalized biradicals, with the precise major reaction pathway depending on the relative concentrations of NO, NO_2 or H_2O (Atkinson and Lloyd, 1984).

Hence, O_3-alkene reactions in the atmosphere can lead ultimately to the formation of aldehydes and acids, as well as to the conversion of SO_2 to H_2SO_4, although the latter is probably a minor process in the overall oxidation of SO_2 during long-range transport (Finlayson-Pitts and Pitts, 1982).

Isoprene and monoterpenes are alkenes emitted from vegetation. The role of these compounds in photochemical air pollution has been a subject of discussion, and sometimes controversy, for more than a decade. The case of ozone reactions with compounds such as isoprene and the monoterpenes is particularly interesting since these reactions can represent a sink for ozone as well as for the hydrocarbons themselves. This adds complexity to an overall assessment of the role of hydrocarbons emitted from vegetation since, depending upon the specific atmospheric conditions, they may be both sources and sinks for ozone (Dimitriades, 1981; Altshuller, 1983).

Again, as in the case of their OH radical reactions, the detailed reaction sequences following reaction of O_3 with iosprene and the monoterpenes are not well understood although substantial kinetic data are available (Atkinson and Carter, 1984); thus only a brief summary of available information is presented here.

Isoprene. The reaction of O_3 with isoprene (Kamens et al., 1982; Lloyd et al., 1983; Killus and Whitten, 1984) leads to molozonides that are presumed to decompose subsequently into stable products and radical intermediates analogous to those produced in other ozone-alkene reactions described earlier in this section. The major products, methlvinylketone and methacrolein, undergo further reactions with OH radicals and ozone (Lloyd et al., 1983; Killus and Whitten, 1984).

The reaction of ozone with isoprene can also lead to aerosol formation (Kamens et al., 1982) and this is discussed in Section 3.3.4.

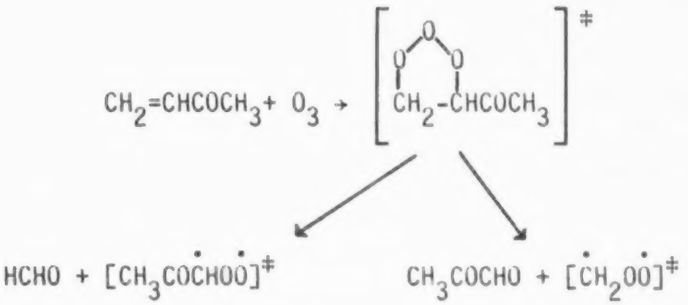
Monoterpenes. The detailed pathway for the reaction of O_3 with the monoterpenes under atmospheric conditions is unknown. Lloyd et al. (1983) have proposed a reaction sequence for α-pinene involving addition of O_3 to the double bond to form a molozonide, with subsequent ring opening. They note, however, that this reaction sequence is entirely speculative, and many additional kinetic and mechanistic data will be required to elucidate the detailed reactions of O_3 with the monoterpenes.

3.3.2.2.2 Alkanes and Alkynes. Given reported rate constants of 10^{-23} to 10^{-26} cm^3 $molecule^{-1}$ sec^{-1} (Atkinson and Carter, 1984), there appears to be no convincing evidence in the literature for an elementary reaction between O_3 and the alkanes. Similarly, although there is presently substantial uncertainty concerning the rate constants for the reactions of ozone with the simple alkynes (e.g., acetylene, propyne and 1-butyne), most of the available room temperature data for these $\leq C_4$ alkynes indicate O_3 rate constants in the range of $\sim 10^{-20}$ to 10^{-19} cm^3 $molecule^{-1}$ sec^{-1} (Atkinson and Carter, 1984). Thus, those reactions will also be unimportant in the atmosphere since the corresponding OH radical rate constants are, for example, $\sim 8 \times 10^{-13}$ for acetylene and $\sim 7 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} for propyne and 1-butyne (Atkinson, 1985).

3.3.2.2.3 Aromatics. As in the case of the alkanes, the aromatic hydrocarbons react only very slowly with O_3 (Atkinson and Carter, 1984) and these reactions are not expected to be important in the atmosphere. Although the cresols are significantly more reactive than the aromatic hydrocarbons (Atkinson and Carter, 1984), under atmospheric conditions their reactions with O_3 are minor compared to their reactions with OH radicals (Atkinson et al., 1978) or NO_3 radicals (Carter et al., 1981a).

3.3.2.2.4 Oxygen-Containing Organics. For those oxygen-containing compounds that contain no unsaturated carbon-carbon bonds (e.g., formaldehyde, acetaldehyde, glyoxal, and methylglyoxal) the reactions with ozone are very slow, and, by analogy, this is expected to be the case for all ethers, alcohols, aldehydes, and ketones containing no unsaturated carbon-carbon bonds. For the carbonyls and ethers (other than ketene) that contain unsaturated carbon-carbon bonds, however, much faster reactions are observed (Atkinson and Carter, 1984).

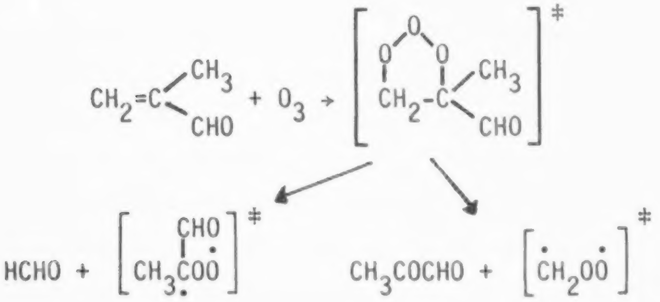
Few data are available, however, concerning the mechanisms of the reactions of O_3 with such oxygen-containing organics, the only published information being that of Kamens et al. (1982). From a study of the reactions of O_3 with methacrolein and methylvinylketone, methylglyoxal was observed as a product, along with other minor products (Kamens et al., 1982), as anticipated from the reaction schemes:



(3-62)

(3-63)

and



(3-64)

Kamens et al. (1982) discuss the possible subsequent reactions.

3.3.2.2.5 Nitrogen-Containing Organics. Studies of the kinetics of the reactions of O_3 with a variety of nitrites, nitriles, nitramines, nitrosoamines, amines, and hydrazines (Atkinson and Carter, 1984) indicate that only for the hydrazines are reactions with O_3 sufficiently rapid to be of atmospheric importance (Carter et al., 1981b; Tuazon et al., 1982).

3.3.2.2.6 Sulfur-Containing Organics. Based upon the kinetic data available for dimethyl sulfide, thiirane (C_2H_4S) and thiophene, it appears at the present time that the rates of reaction of O_3 with sulfur-containing organics can be considered to be unimportant under atmospheric conditions (Atkinson and Carter, 1984).

3.3.2.2.7 Organometallics. Rate constants have been reported only for tetramethyl- and tetraethyl-lead (Harrison and Laxen, 1978), and no mechanistic or product data are available for these reactions.

3.3.2.2.8 Radical Species. Because of the low concentration of O_3 and of both alkyl and most alkoxy radicals in the atmosphere, and because these radicals react at significant rates with O_2 (which is present at a concentration $>10^5$ higher than O_3 in ambient atmospheres), the reactions of ozone with such radical species can be considered to be of negligible importance in the atmosphere. Of course, the reaction of ozone with the hydroxyl radical must be considered, as discussed earlier.

3.3.2.3 Reactions with Nitrate Radicals. The pioneering work of Niki and coworkers (Morris and Niki, 1974; Japar and Niki, 1975) showed that gaseous NO_3 radicals react with alkenes, with the rate constants increasing markedly with the degree of substitution on the double bond. Carter et al. (1981a) showed that the hydroxy-substituted aromatics (phenols and the cresols) also react rapidly with NO_3 radicals.

More recently, Atkinson and coworkers have investigated the kinetics of the reactions of NO_3 radicals with a wide range of organics at room temperature (Atkinson et al., 1984a-e) and from these and the earlier studies, information concerning the mechanisms of these reactions has been forthcoming.

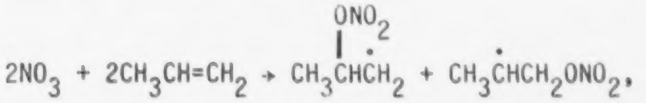
In the remainder of this section, current understanding of the mechanisms of reaction of NO_3 radicals with the various classes of organics is briefly summarized.

3.3.2.3.1 Alkanes. The relevant kinetic data (Atkinson et al., 1984e) indicate that these reactions proceed via H-atom abstraction from the C-H bonds, almost certainly predominantly from secondary or tertiary C-H bonds:

$$NO_3 + RH \rightarrow HNO_3 + R^{\bullet} \qquad (3\text{-}65)$$

Hence, these reactions lead directly to HNO_3 formation. The measured room temperature rate constants for the alkenes range between 3.6×10^{-17} cm^3 $molecule^{-1}$ sec^{-1} for n-butane to 2.2×10^{-16} cm^3 $molecule^{-1}$ sec^{-1} for 2,3-dimethylbutane.

3.3.2.3.2 Alkenes. The reactions of NO_3 radicals with the alkenes have been shown from both kinetic (Japar and Niki, 1975; Atkinson et al., 1984a) and product (Bandow et al., 1980) studies to proceed via initial addition of the NO_3 radical to the olefinic double bond:



$$2NO_3 + 2CH_3CH{=}CH_2 \rightarrow CH_3\overset{\overset{\displaystyle ONO_2}{|}}{C}H\dot{C}H_2 + CH_3\dot{C}HCH_2ONO_2, \qquad (3\text{-}66)$$

with addition at the terminal carbon expected to dominate (Atkinson and Lloyd, 1984). Possible reaction sequences beyond this initial reaction have been discussed (Bandow et al., 1980; Atkinson and Lloyd, 1984) but are highly uncertain at the present time (Atkinson and Lloyd, 1984).

Thermally unstable nitro-peroxynitrates such as $CH_3CH(ONO_2)CH_2OONO_2$, and stable dinitrates such as $CH_3CH(ONO_2)CH_2ONO_2$ have been reported as products in NO_3-NO_2-propene-air systems (Bandow et al., 1980).

Monoterpenes. While no mechanistic information is available concerning the reactions of NO_3 radicals with the monoterpenes, NO_3 radical reaction rate constants have recently been reported for a substantial number of these compounds (Atkinson et al., 1984c, 1985). Based in part on these kinetic data, Winer et al. (1984) have proposed that reaction with NO_3 radicals at night may be an important reaction pathway for certain naturally occurring organics such as the monoterpenes and dimethyl sulfide. Conversely, these kinetic data also show that reactions with the more reactive alkenes, including isoprene and certain of the monoterpenes, as well as dimethyl sulfide and the hydroxy-substituted aromatics, can be important loss processes for NO_3 radicals at night (Winer et al., 1984). The importance of NO_3 radical reactions in determining the atmospheric lifetimes of the monoterpenes is discussed in section 3.3.3.

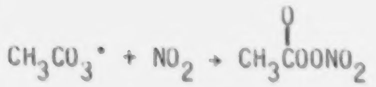
3.3.2.3.3 Aldehydes. Based upon the product data of Morris and Niki (1974), i.e., the observed formation of HNO_3 from the reaction of NO_3 radicals with CH_3CHO, it is expected that these reactions proceed via H-atom abstraction from the relatively weak H-CO bonds:

$$NO_3 + RCHO \rightarrow R\dot{C}O + HNO_3 \tag{3-67}$$

Thus the reaction of NO_3 radicals with acetaldehyde could be a nighttime source of peroxyacetyl nitrate (PAN):

$$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3\dot{C}O \tag{3-68}$$

$$CH_3\dot{C}O + O_2 \rightarrow CH_3CO_3^{\bullet} \tag{3-69}$$

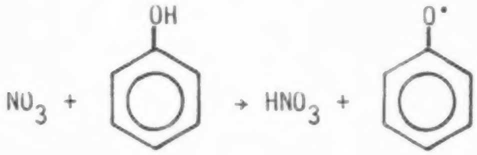


$$CH_3CO_3^{\bullet} + NO_2 \rightarrow CH_3\overset{\overset{O}{\|}}{C}OONO_2 \tag{3-70}$$

Reaction of NO_3 radicals with the higher aldehydes will lead, by analogous reaction schemes, to the higher peroxyacyl nitrates, RCO_3NO_2. Reaction with formaldehyde, however, will lead to HO_2 radical formation, since HCO reacts rapidly with O_2 (Atkinson and Lloyd, 1984):

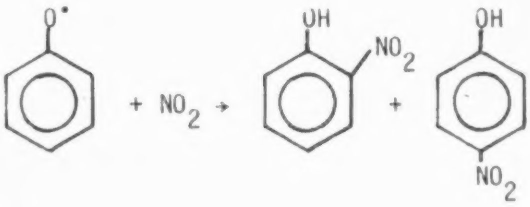
$$HCO + O_2 \rightarrow HO_2 + CO \qquad (3\text{-}71)$$

3.3.2.3.4 Aromatics. As discussed by Atkinson et al. (1984d), the reactions of NO_3 radicals with the monocyclic aromatic hydrocarbons and the hydroxy-substituted aromatics appear, based upon kinetic evidence, to proceed via H-atom abstraction from the C-H or O-H bonds on the substituent groups. This conclusion is based upon the observation that for the xylenes and the cresols the meta-isomer reacts more slowly (by a factor of ~2) than the ortho- and para-isomers. This is in contrast to the addition reactions of $O(^3P)$ atoms and OH radicals, in which the meta-isomer is the most reactive (Atkinson, 1985). Furthermore, *o*-nitrophenol has been tentatively identified as a product of N_2O_5-NO_2-phenol-air reaction mixtures, presumably formed by the reaction sequence:



(3-72)

followed by (Niki et al., 1979):



(3-73)

Thus, these reactions can also be a direct source of nitric acid as well as forming low-volatility organic nitro compounds.

In summary, it is now clear that reaction with NO_3 radicals at night is a major atmospheric reaction pathway for many organic pollutants. It must therefore be considered, along with the reactions of OH radicals and O_3 and photolysis, as one of the dominant loss processes for organics in the atmosphere.

3.3.3 Atmospheric Lifetimes of Organic Compounds

Table 3-6 compares the atmospheric lifetimes (i.e., the time to reach 1/e of the initial concentration) for selected organic compounds, arising from manmade and natural sources, as the result of reaction with O_3 over a 24-hour period, with OH radicals during the day, and with NO_3 radicals at night. It can be seen that under the atmospheric conditions assumed reactions with O_3 are important for the higher alkenes, including the monoterpenes during daylight when NO_3 radical concentrations are low, and for the hydrazines. For the other organics for which kinetic data are available, including alkanes and aromatics, reactions with O_3 are generally of negligible or minor importance in determining their atmospheric lifetimes.

TABLE 3-6. CALCULATED LIFETIMES OF SELECTED ORGANIC COMPOUNDS RESULTING FROM ATMOSPHERIC LOSS BY REACTION WITH O_3 AND OH AND NO_3 RADICALS

Organic compound	Organic lifetimes[a,b]		
	O_3, 24 hr	OH, daytime	NO_3, nighttime
Alkenes from manmade sources			
Ethene	2.7 days	16 hr	79 days
Propene	11 hr	5.6 hr	1.1 days
trans-2-Butene	35 min	2.0 hr	33 min
2-Methyl-2-butene	17 min	1.6 hr	1.3 min
2,3-Dimethyl-2-butene	6 min	1.3 hr	0.2 min
Naturally emitted alkenes			
Isoprene	10 hr	1.4 hr	22 min
α-Pinene	1.4 hr	2.3 hr	2 min
β-Pinene	5.5 hr	1.8 hr	5 min
Δ^3-Carene	1.0 hr	1.7 hr	1.2 min
d-Limonene	11 min	1.0 hr	0.9 min

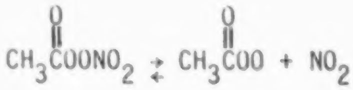
[a] Time to reach 1/e of the initial concentration.

[b] Assuming 100 ppb of O_3 (24 hr average), 2×10^6 molecule cm^{-3} (0.08 ppt) of OH radicals during daylight hours, and 100 ppt of NO_3 radicals during nighttime hours, and at room temperature.

3.3.4 Atmospheric Reactions of Peroxyacetyl Nitrate

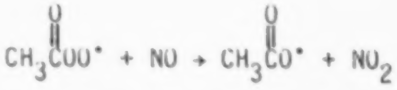
With the recognition in recent years that PAN is a ubiquitous nitrogenous species in the troposphere (Singh and Hanst, 1981; Aikin et al., 1983; Penkett, 1983; Singh and Salas, 1983; Spicer et al., 1983) and in the lower stratosphere (Aikin et al., 1983), there has been renewed focus on the atmospheric role of this organic compound.

Smog chamber studies have shown that, once formed, PAN can be relatively stable under atmospheric thermal conditions (Pitts et al., 1979; Akimoto et al., 1980). Since PAN is in equilibrium, however, with acetylperoxy radicals and NO_2:

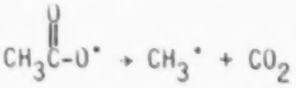


$$CH_3\overset{\overset{O}{\|}}{C}OONO_2 \rightleftarrows CH_3\overset{\overset{O}{\|}}{C}OO + NO_2 \qquad (3\text{-}74)$$

any process that removes either acetyl peroxy radicals or NO_2 will lead to the decomposition of PAN. One such process is the reaction of NO with $CH_3C(O)O_2$ radicals. Because PAN has been shown to persist through the night in urban atmospheres (Tuazon et al., 1980, 1981a) the reaction of PAN with NO during the morning traffic peak can lead to the formation of OH radicals via the following mechanism (Cox and Roffey, 1977; Carter et al., 1981c):



$$CH_3\overset{\overset{O}{\|}}{C}OO^{\cdot} + NO \rightarrow CH_3\overset{\overset{O}{\|}}{C}O^{\cdot} + NO_2 \qquad (3\text{-}75)$$



$$CH_3\overset{\overset{O}{\|}}{C}\text{-}O^{\cdot} \rightarrow CH_3^{\cdot} + CO_2 \qquad (3\text{-}76)$$

$$CH_3^{\cdot} + O_2 \xrightarrow{M} CH_3OO \qquad (3\text{-}77)$$

$$CH_3OO^{\cdot} + NO \rightarrow CH_3O^{\cdot} + NO_2 \qquad (3\text{-}78)$$

$$CH_3O^{\cdot} + O_2 \rightarrow HO_2 + HCHO \qquad (3\text{-}79)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (3\text{-}80)$$

$$OH + NO \xrightarrow{M} HONO \qquad (3\text{-}81)$$

$$\dot{O}H + NO_2 \xrightarrow{M} HNO_3 \qquad (3\text{-}82)$$

Thus, the reaction with NO of PAN carried over from previous air pollution episodes will lead to enhanced smog formation on subsequent days. This enhancement in reactivity results both from the fact that these reactions form radicals that initiate the transformations occurring in photochemical smog and from the fact that these reactions convert NO to NO_2, which allows earlier formation of O_3 and higher levels to be attained. It should be noted that this enhancement will result even if all of the PAN reacts with NO emitted at nighttime, since the NO conversion does not require sunlight and since at least some of the radicals formed will be "stored" as nitrous acid, to be released when photolysis begins at sunrise (Harris et al., 1982).

These results could have important implications regarding multiday photochemical pollution episodes in which significant buildup of PAN is observed. Under such conditions, the carry-over of PAN may be a significant factor in promoting ozone formation on subsequent days and may, in part, contribute to the progressively higher O_3 levels often observed during such episodes (Tuazon et al., 1981a).

A second important role of PAN is its ability to contribute to the long-range transport of NO_x. In the absence of significant levels of NO (i.e., in the cleaner troposphere) and in regions of lower temperature and in the upper troposphere, when the thermal decomposition of PAN becomes unimportant, the atmospheric lifetime of PAN will be determined by its reaction with OH radicals. This reaction is sufficiently slow (Wallington et al., 1984) that PAN will probably be long-lived and hence serve as a reservoir for odd nitrogen in a manner analogous to HNO_3 (Aikin et al., 1983). Also analogous to the case for HNO_3, dry deposition of PAN may be a significant loss process in cleaner atmospheres.

3.3.5 Role of Ozone in Aerosol Formation

In addition to having direct effects on human health and on vegetation, ecosystems, and nonbiological materials, ozone can contribute indirectly to visibility degradation and to acidic deposition through its participation in the formation of both organic and inorganic aerosols (National Research Council, 1977a; U. S. Environmental Protection Agency, 1982b).

3.3.5.1 Formation of Sulfate Aerosol. It is well established that the source of the vast majority of manmade sulfate aerosol in the atmosphere is the oxidation of sulfur dioxide (SO_2), ultimately to sulfuric acid (H_2SO_4). The correlations between elevated levels of ozone and of sulfate aerosol in ambient air have been noted by several investigators in field studies concerned with visibility reduction by aerosols. Wilson (1978) and Gillani et al. (1981) have pointed out that atmospheric mixing intensity and the background O_3 concentration are the two most important factors in determining SO_2 oxidation at relative humidities lower than 75 percent. It is also clear, however, that the rate of reaction of O_3 with SO_2 is far too slow to account for observed formation rates of sulfate aerosol (U. S. Environmental Protection Agency, 1982b).

Of the many possible gas-phase reactions of SO_2, only a few appear to have any significance in the production of sulfate aerosol and the reaction of OH radicals with SO_2 appears to be the dominant pathway for the oxidation of SO_2 (Calvert and Stockwell, 1983, 1984; Calvert and Mohnen, 1983). A recent analysis by Stockwell and Calvert (1983) shows that the formation of $HOSO_2$ radicals from the reaction of OH radicals with SO_2, followed by reaction with O_2, is the reaction mechanism for the formation of SO_3:

$$OH + SO_2\ (+\ M) \rightarrow HOSO_2\ (+\ M); \qquad (3\text{-}83)$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3. \qquad (3\text{-}84)$$

From the reaction of HO_2 radicals with NO, OH radicals are regenerated and the cycle begins again as discussed earlier in Section 3.3.1.2.1.

The importance of the reaction of OH radicals with SO_2 in the atmosphere is supported by observations of power plant plumes, in which no aerosol is formed at night when the OH radical concentration in ambient air is negligible; and none is formed during the day before the plume is well mixed with ambient air (the ambient air contains much higher concentrations of OH radicals and O_3 than the plume) (Davis et al., 1979; Blumenthal et al., 1981).

Though it does not react directly with SO_2 at an appreciable rate, by virtue of its role in OH radical production O_3 plays an important indirect role in the transformation of SO_2 to sulfate aerosol via the homogeneous oxidation of SO_2 in both clean and polluted atmospheric systems. Ozone plays a further role in the oxidation of sulfur in aqueous droplets as discussed later in this section.

3.3.5.2 Formation of Nitrate Aerosol. Despite limited relevant data, the possible contribution of nitrate aerosol to visibility reduction should not be neglected and the role of O_3 in the formation of this aerosol species is briefly considered here.

The principal manmade nitrogen emissions in this case are NO and NO_2. Nitric oxide is relatively insoluble in aqueous systems (Section 3.2) and does not react with water in any significant manner. Thus, NO must be converted to a more highly oxidized form, for example NO_2, in order to participate in the formation of particulate nitrate.

The oxidation of NO to NO_2 can occur through thermal oxidation at high concentrations of NO such as those in and very near the stacks of power plants (U. S. Environmental Protection Agency, 1982a). This generates only a small portion of the NO_2 formed in the atmosphere, however. As previously discussed (Section 3.3.1), the most important reactions leading to formation of NO_2 in ambient air are the reaction of NO with O_3 and the oxidation of NO to NO_2 by hydroperoxyl radicals and other peroxy radicals (reactions 3-3 and 3-11, respectively). Thus, if NO_2 is a precursor of nitrate aerosol, O_3 plays a significant direct role in its formation by oxidizing NO, and an indirect role by leading to formation of OH radicals (Section 3.3.1).

As discussed earlier, NO_2 can be converted in the gas phase to nitric acid (HNO_3) vapor by reaction with OH radicals during the day or by

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As discussed earlier, NO_2 can be converted in the gas phase to nitric acid (HNO_3) vapor by reaction with OH radicals during the day or by reaction with O_3 to form NO_3 radicals, which at night are in equilibrium with N_2O_5. As shown in Section 3.3.1.5, homogeneous or heterogeneous hydrolysis, or both, of N_2O_5 is an important nighttime pathway to nitric acid formation. Once it has been produced in the gas phase, HNO_3 is sufficiently volatile to remain in the atmosphere as a vapor. The available laboratory and ambient air data indicate, however, that HNO_3 vapor reacts with ammonia in a reversible reaction to form NH_4NO_3 (Doyle et al., 1979; Stelson et al., 1979; Appel et al., 1980), which, because of its low vapor pressure, will form nitrate aerosol particles:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{3-85}$$

If acidic sulfate is present, however, it will react with NH_4NO_3 to form HNO_3 again. Consequently, reaction (3-85) is not a major sink for nitric acid in areas with high sulfate loading, such as the eastern United States. Evidence also indicates that HNO_3 vapor will react with NaCl aerosol in the following way:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \tag{3-86}$$

This second reaction (equation 3-86) may account for the fact that much of the observed particulate nitrate in Los Angeles is found in the coarse mode (Farber et al., 1982). Obviously, the importance of this mechanism for nitrate aerosol formation is determined by the availability of sea salt particles.

3.3.5.3 Formation of Organic Aerosols. Sulfate and nitrate aerosols are present at significant levels in the atmosphere in the form of just a few compounds. In contrast, secondary organic aerosols are composed of a large number of species, but there is no clear consensus concerning which ones contribute most to the mass concentration. For all the species that are found in the secondary organic aerosol, however, the fundamental formation mechanism is the same. The vapor-phase precursor undergoes some reaction that results in formation of a product having an equilibrium vapor pressure sufficiently low that condensation, nucleation, or both are possible at the gaseous concentration achieved. From the available data, it seems clear that the more highly oxygenated, larger-carbon-number species generally are those precursors likely to form secondary aerosols in the atmosphere.

For an earlier but thorough review of the formation of secondary aerosol, the reader is referred to the 1977 monograph on ozone and other photochemical oxidants prepared by the National Research Council (1977a). This monograph reviews the reactions of manmade volatile organic compounds that produce aerosol. Biogenic as well as manmade volatile organic compounds, however, can participate in aerosol formation (Altshuller and Bufalini, 1971; Arnts and Gay, 1979). Direct experimental evidence of aerosol formation, along with product analysis, is only available, though, for a limited number of natural compounds, including isoprene (Kamens et al., 1982) and α-pinene and β-pinene (Schwartz, 1974; National Research Council, 1977a; Hull, 1981), mainly because the analysis and characterization of these kinds of products at ambient concentrations is extremely difficult. Hull (1981) has conducted experiments with α- and β-pinene at high concentrations in a small tube reactor. Analysis of the products showed, on a weight basis, that almost all of the reacted α-pinene carbon was found in the condensed materials extracted from the walls. Although the products identified from these experiments were either in the condensed phase or on the walls, Hull suggested that at the α-pinene levels found in ambient air these products have a high enough vapor pressure to exist both in the gas phase and in aerosols (Hull, 1981). In a recent review of the role of biogenic volatile organic compounds, Altshuller (1983) has discussed at length the contribution of these compounds to ambient air aerosols.

3.3.6 Role of Ozone and Other Photochemical Oxidants in the Acidification of Rain

Two recent criteria documents prepared by the U. S. Environmental Protection Agency (1982a; 1982b) contain thorough discussions of the contributions of ozone and of hydrogen peroxide, also an oxidant, to the oxidation of SO_2 and the roles of SO_2 as a precursor to acidic deposition.

3.3.6.1 Reactions of Ozone in Aqueous Droplets. While the thermal oxidation of SO_2 by ozone in the gas phase appears to be too slow to be important in acid deposition phenomena, the role of ozone in oxidizing SO_2 dissolved in water droplets (e.g., cloud, fog or rain) may be of considerable significance. At 25°C ozone has a Henry's law constant of 10^{-2} mol L^{-1} atm^{-1} (Kirk-Othmer, 1981). Given ambient concentrations ranging from 30 to ~300 ppb, O_3 would be expected to have concentrations in aqueous droplets in the atmosphere of approximately 3-30 x 10^{-10} mol L^{-1}. The rate of reaction between O_3 and SO_2, when both are dissolved in aqueous droplets, has been shown in laboratory studies to be relatively fast (Penkett et al., 1979; Kunen et al., 1983; Brock and Durham, 1984; Hoffman and Jacob, 1984; Martin, 1984; Schwartz, 1984), but the rate of this reaction is pH dependent and decreases as the acidity of the solution increases.

Figure 3-3 shows data reported by Schwartz (1984) for the rate of the aqueous-phase oxidation of S(IV) by 30 ppb of O_3 (and also by 1 ppb of H_2O_2) as a function of solution pH. The aqueous-phase oxidation rate, R, per part-per-billion SO_2 partial pressure decreases with decreasing pH by roughly a factor of 20 per pH unit. This pH dependence reflects the solubility of S(IV), as well as a slight pH dependence of the second-order rate constant for the oxidation of S(IV) by O_3 (Erickson et al., 1977; Larson et al., 1978; Penkett et al., 1979). Schwartz (1984) concluded, from consideration of these data and uptake times for SO_2, that the oxidation of SO_2 by O_3 cannot produce solution pH values below ~4.5. Schwartz (1984) has also, however, interpreted the field data of Hegg and Hobbs (1981) for sulfate production rates at the inflow and outflow regions of lenticular clouds as being consistent with the aqueous phase oxidations of S(IV) by O_3.

An additional aspect of the role of O_3 in the chemistry of aqueous droplets concerns its photolysis to yield OH radicals in solution (Graedel and Weschler, 1981; Chameides and Davis, 1982):

$$(O_3)_{aq} + h\nu \rightarrow O(^1D)_{aq} + O_{2\ aq} \tag{3-87}$$

$$O(^1D)_{aq} + (H_2O)_{aq} \rightarrow 2(OH)_{aq} \tag{3-88}$$

and its reactions with aqueous OH^- ions and H_2O_2 to yield aqueous HO_2 radicals (Chameides and Davis, 1982). The OH radicals formed by this aqueous process can result in the oxidation of S(IV).

3.3.6.2 Reactions of Hydrogen Peroxide in Aqueous Droplets. lthough hydrogen peroxide formed in the gas phase from the reactions of

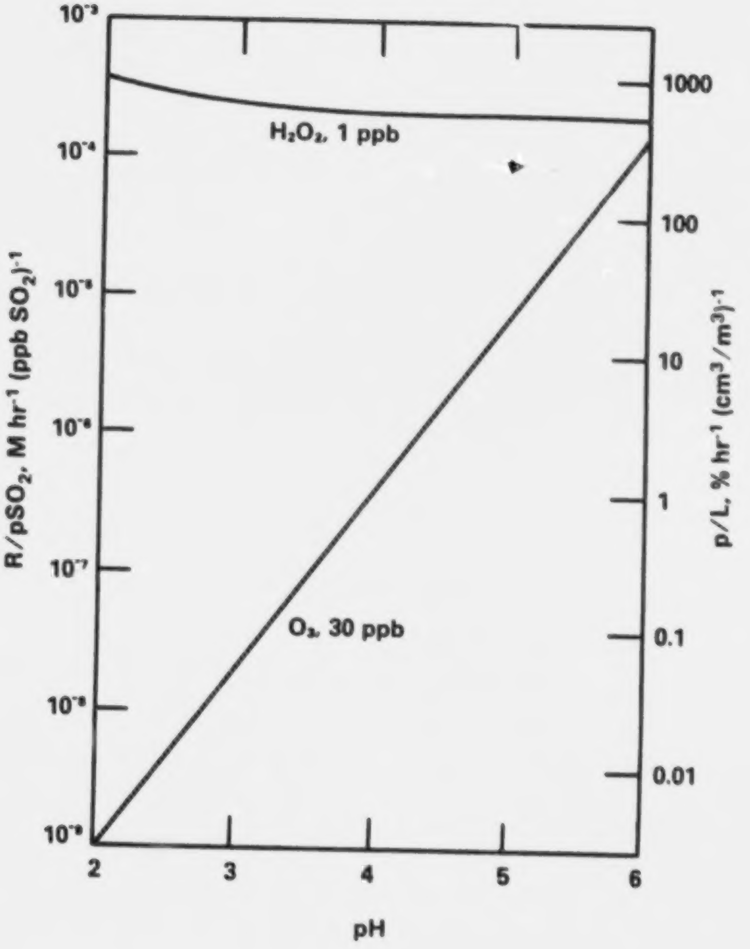

Figure 3-3. Rate of aqueous-phase oxidation of S(IV) by O_3 (30 ppb) and H_2O_2 (1 ppb), as a function of solution pH. Gas-aqueous equilibria are assumed for all reagents. R/pSO_2 represents aqueous reaction rate per ppb of gas-phase SO_2; p/L represents rate of reaction referred to gas-phase SO_2 partial pressure per cm^3—m^{-3} liquid water volume fraction.

Source: Schwartz (1984).

hydroperoxyl radicals plays a role in HO_x chemistry in the troposphere, and especially in the stratosphere (Crutzen and Fishman, 1977; Cox and Burrows, 1979), the major importance of hydrogen peroxide arises from its high solubility in water. The latter ensures that a large fraction of gaseous H_2O_2 will be taken up in aqueous droplets. Over the past decade, evidence has accumulated that H_2O_2 dissolved in cloud, fog, and rainwater may play an important, and, in acidic droplets (i.e., pH $\lesssim 5$), even a dominant role in the oxidation of SO_2 to H_2SO_4 (Hoffman and Edwards, 1975; Penkett et al., 1979; Dasgupta 1980a,b; Graedel and Weschler, 1981; Martin and Damschen, 1981; Chameides and Davis, 1982; Calvert and Stockwell, 1983, 1984; Brock and Durham, 1984; Hoffman and Jacob, 1984; Schwartz, 1984). Discussion of several proposed mechanisms for previous rate studies of the oxidation of S(IV) by H_2O_2 are beyond the scope of this document, but have recently been reviewed by several authors (see for example, Calvert and Stockwell, 1983, 1984). Hydrogen peroxide may also play a role in the oxidation of NO_2 dissolved in aqueous droplets, although relevant data are limited (Halfpenny and Robinson, 1952a,b; Anbar and Taube, 1954; Gertler et al., 1984) and additional research is required. In addition to the direct oxidation of SO_2 and NO_2 dissolved in aqueous droplets, the photolysis of H_2O_2 to produce aqueous OH radicals:

$$(H_2O_2)_{aq} + h\nu \rightarrow 2(OH)_{aq} \tag{3-89}$$

can lead to oxidation rates of S(IV) that can be competitive with calculated oxidation rates of S(IV) by $(H_2O_2)_{aq}$ and $(O_3)_{aq}$ (Chameides and Davis, 1982).

It should be emphasized, however, that substantial uncertainties remain concerning the quantitative role of H_2O_2 in the acidification of aqueous particles and droplets (Richards et al., 1983). This is further complicated by the lack of reliable measurements of gas-phase H_2O_2 concentrations in the atmosphere (see Chapter 4). Moreover, it has also been suggested recently that H_2O_2 may be formed in situ in aqueous droplets as the result of absorption of OH and HO_2 radicals and other precursors into solution from the gas phase (Graedel and Weschler, 1981; Chameides and Davis, 1982; Heikes et al., 1982).

3.3.6.3 Reactions of Formic Acid in Aqueous Droplets. As a gas-phase species, formic acid (HCOOH) cannot strictly be defined as a photochemical oxidant. It can be scavenged rapidly into water droplets, however, and can potentially function therefore as an oxidant in cloud water and rain water. It can also be differentiated from other acids in that it is formed readily from the reactions of the Criegee intermediates discussed earlier and of hydroperoxyl radicals with formaldehyde (Calvert and Stockwell, 1983). The formation of other acids may be orders of magnitude slower as the result of both the apparently lower rates of reaction of HO_2 radicals with the higher aldehydes and the much lower atmospheric concentrations of the higher aldehydes (Grosjean, 1982). Thus, formic acid is an example of a compound that is a non-oxidant or weak oxidant in the gas phase but that is transformed upon incorporation in aqueous solutions into an effective oxidizer of S(IV).

Formic acid (as well as acetic acid) has been identified among the acidic components of rain (Galloway et al., 1982). Although much uncertainty remains concerning their quantitative roles, HCOOH and the higher organic acids potentially play a minor but still significant role in the acidification of rain.

3.4 METEOROLOGICAL AND CLIMATOLOGICAL PROCESSES

As discussed in Section 3.3, ozone and oxidants are formed by the action of sunlight on the precursors, NO_2 and hydrocarbons. The accumulation of the products to form an appreciable concentration is also dependent, however, on the prevailing meteorology in the vicinity of the precursor emissions. To understand the details of the effects of meteorology on air quality requires a thorough knowledge of meteorology and climatology, but an appreciation of the general factors important in the formation of elevated concentrations of oxidants is relatively easy to acquire. Following is a brief presentation of some features of atmospheric mixing and transport that will provide a basic understanding of the meteorological factors that affect the concentrations of ozone and other oxidants in urban and rural areas.

3.4.1 Atmospheric Mixing

The concentration of an air pollutant depends significantly on the degree of mixing that occurs between the time a pollutant or its precursors are emitted and the arrival of the pollutant at the receptor. Since, to a first approximation, the diurnal cycle of weekday urban emission patterns for ozone and oxidant precursor pollutants is generally uniform, it is reasonable to ascribe a significant proportion of the large day-to-day changes in pollutant concentrations to changes in meteorological mixing processes. The rate at which atmospheric mixing processes occur and the extent of the final dilution of the pollutants depends on the amount of turbulent mixing and on wind speed and wind direction. Moreover, the transport of pollutants and precursors from a source region to a distant receptor is also dependent on wind speed and wind direction.

The degree of turbulent mixing can be characterized by atmospheric stability. In an atmospheric layer with relatively low turbulence, pollutants do not spread as rapidly as they do in an unstable layer. Also, because a stable layer has a relatively low rate of mixing, pollutants in a lower layer will not mix through it to higher altitudes. The stable layer can act as a trap for air pollutants lying beneath it. Hence, an elevated inversion is often referred to as a "trapping" inversion. Also, if pollutants are emitted into a stable layer aloft, such as from a stack, the lack of turbulence will keep the effluents from reaching the ground while the inversion persists.

In air pollution considerations, a stable atmospheric layer or situation is usually equated with a temperature inversion, which is a layer of the atmosphere in which the temperature increases with increasing altitude, because inversions are common and also represent the most stable atmospheric conditions. The lowest part of an inversion layer is called the base and is defined as the altitude at which the temperature begins to increase. The top of the inversion is the point at which the temperature begins to decrease with increasing altitude. The distance between the base and top of the inversion layer is the "depth" or "thickness" of the inversion. Inversion layers may begin at the ground surface (i.e., the altitude of the base is zero), or the entire inversion layer may be above the surface. The former is known as a "surface inversion" and the latter as an "elevated inversion." The two types are usually caused by different sets of weather conditions, but it is not unusual for both types of inversions to be present at a given location at the same time. In the United States, surface inversions are characteristic of nighttime and early morning hours except when heavy cloud cover or windy and stormy conditions prevail.

Surface and elevated inversion layers are both important in determining pollutant concentration patterns since, as noted above, mixing and dilution processes proceed at a relatively slow rate in such layers. Thus, if pollutants are emitted into an inversion layer, relatively high concentrations can persist for a considerable period of time or over a considerable distance of wind travel from the source. For example, a surface inversion in the morning could cause automotive exhaust pollutants released at the surface during the morning rush hours to persist with minimum dilution near the ground surface for an extended period of time, probably for 1 or 2 hours after sunrise, until solar radiation heats the ground and causes the inversion to disappear or "break" (Hosler, 1961; Slade, 1968). High concentrations may occur at the ground even when an elevated inversion is present and the layers below the inversion are unstable and are undergoing good mixing. Such a persistent elevated inversion layer is a major meteorological factor that contributes to high pollutant concentrations and photochemical smog situations along the southern California coast (Holzworth, 1964; Hosler, 1961; Robinson, 1952).

The vertical mixing profile through the lower layers of the atmosphere follows a typical and predictable cycle on a generally clear day. In such a situation a surface inversion would be expected to form during the early morning and to persist until surface heating becomes significant, probably 2 or 3 hours after sunrise. Pollutants initially trapped in the surface inversion may cause relatively high, local concentrations, but these concentrations will decrease rapidly when the surface inversion is broken by surface heating, usually about midmorning. The surface inversion will begin to form again during the early evening hours and pollutants from near-surface sources such as automobiles or home fireplace chimneys will experience progressively less dilution as the surface inversion develops.

Elevated inversions, when the base is above the ground, are also common occurrences (Hosler, 1961; Holzworth, 1964). Since these conditions, however, are identified with specific synoptic conditions, they are much less frequent than the nighttime radiation inversion. Because it may persist throughout the day and thus restrict vertical mixing, an elevated inversion is nevertheless a very significant air pollution feature. Smog-plagued southern California is adversely affected by persistent elevated inversions (Robinson, 1952). When compared to a source near the surface and the effects of a radiation (surface) inversion, the pollutant dispersion pattern is quite different for an elevated source plume trapped in a layer near the base of an elevated inversion. This plume will not be in contact with the ground surface in the early morning hours because there is no mixing downward through the surface radiation inversion. Thus, the elevated plume will not affect surface pollutant concentrations until the mixing processes become strong enough to reach the altitude of the plume. At that time, the plume may be mixed downward quite rapidly in a process called "fumigation." During fumigation, surface ozone concentrations will increase if the morning ozone concentration is higher aloft than at the ground, and if insufficient scavenging by NO occurs at ground-level. After this initial mixing, surface concentrations will decrease as the usual daytime mixing processes continue to develop. If the daytime mixing becomes strong enough to break the upper inversion, the pollutants may be mixed through an increasingly deep layer of the atmosphere. When surface heating decreases in the late afternoon and early evening, both the surface and elevated inversions will form again. The surface inversion will again prevent pollutants from elevated sources from reaching the ground and surface scavenging processes will gradually reduce the concentrations of pollutants trapped during the formation of the surface inversion.

Geography can have a significant impact on dispersion of pollutants (e.g., along the coast of an ocean or one of the Great Lakes). Near the coast or shore, the temperatures of land and water masses can be different, as can the temperature of the air above such land and water masses. When the water is warmer than the land, there is a tendency toward reduction in the frequency of surface inversion conditions inland over a relatively narrow coastal strip (Hosler, 1961). This in turn tends to increase pollutant dispersion in such areas. Such conditions may occur frequently on the Gulf Coast and near the Great Lakes in the winter. The opposite condition also occurs if the water is cooler than the land, as in summer or fall. Cool air near the water surface will tend to increase the stability of the boundary layer in the coastal zone, and thus decrease the mixing processes that act on pollutant emissions. These conditions occur frequently along the New England coast (Hosler, 1961). Similarly, pollutants from the Chicago area have been observed repeatedly to be influenced by a stable boundary layer over Lake Michigan (Lyons and Olsson, 1972). This has been observed especially in summer and fall when the lake surface is most likely to be cooler than the air that is carried over it from the adjacent land.

Since the diurnal mixing conditions are such an important part of the meteorological parameters for understanding pollutant mixing and diffusion, it is useful to have some knowledge of the mixing cycles that prevail over the United States. Figures 3-4 and 3-5 show the average summer morning and afternoon mixing heights (AGL, above ground level) as calculated on the basis of upper air temperature data and an estimated midmorning urban temperature. Since Holzworth (1972) attempted to include the influence of an urban heat island in this estimated temperature, the morning results in Figure 3-4 are probably most applicable to larger urban areas. Rural or nonurban areas would be expected to have lower mixing heights.

Summer conditions are useful to consider because of the prevalence of high photochemical oxidant concentrations during this season. As shown in Figure 3-4, morning mixing heights are estimated to be greater than 300 meters except for the central part of the Great Basin, where a 200-meter isopleth includes parts of Oregon, Idaho, Utah, Arizona, and most of Nevada. By midafternoon (Figure 3-5), the estimated mixing height at the time of maximum temperature has increased markedly, and only a few coastal areas have an average afternoon maximum mixing height of less than 1000 meters. In contrast to the morning data, the central Great Basin area becomes the area of greatest mixing in the afternoon. This would be expected since this is a hot, arid, desert region, and the driving force generating the surface mixing layer is the solar heating of the ground surface.

The magnitude of the afternoon mixing height is generally an indication of the potential for recurring urban air pollution problems. If a trapping, elevated inversion does not rise high enough in the afternoon to release the generated pollutants that are trapped, an accumulating episode is likely. From the average summer afternoon data shown in Figure 3-5, where the lowest average mixing height is 600 meters and almost all of the area has a value greater than 1500 meters, it would appear that urban air pollution should not be severe. On the average this is probably correct; however, there are several departures from the average, which result in relatively low mixing heights and adverse dispersion over many areas of the United States on a recurring basis.

Figure 3-6 (Holzworth and Fisher, 1979) shows the frequency of occurrence of elevated inversions in summer having a base between 1 and 500 meters (1600 feet) at the time of the afternoon upper air temperature measurement, 6:10 p.m. EST or 3:15 p.m. PST. The California coastal conditions, in which low inversions occur with a frequency of nearly 90 percent, are clearly evident. The northeastern coastal area from New Jersey north to Maine, where cool ocean

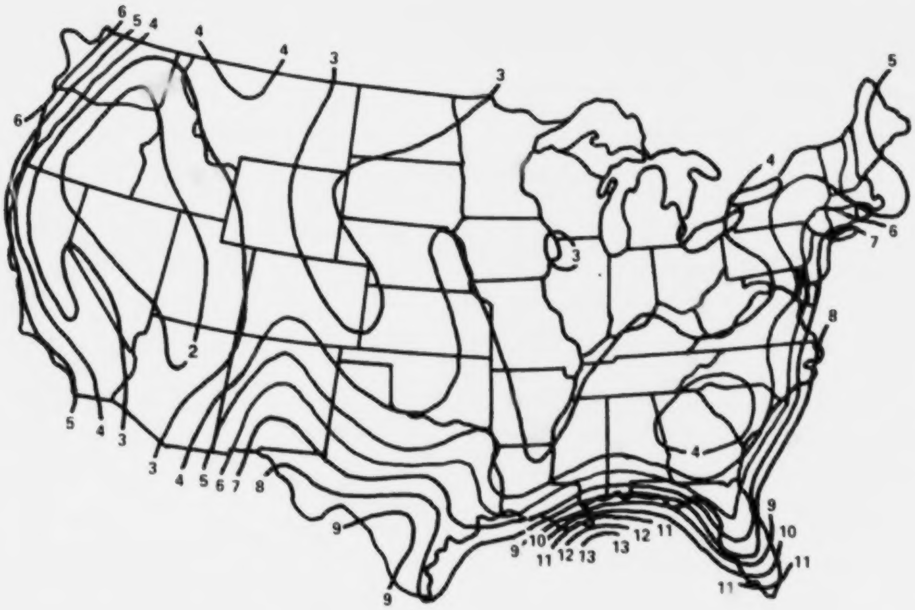
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Figure 3-4. Isopleths (m x 10^2) of mean summer morning mixing heights, AGL.

Source: Holzworth (1972).

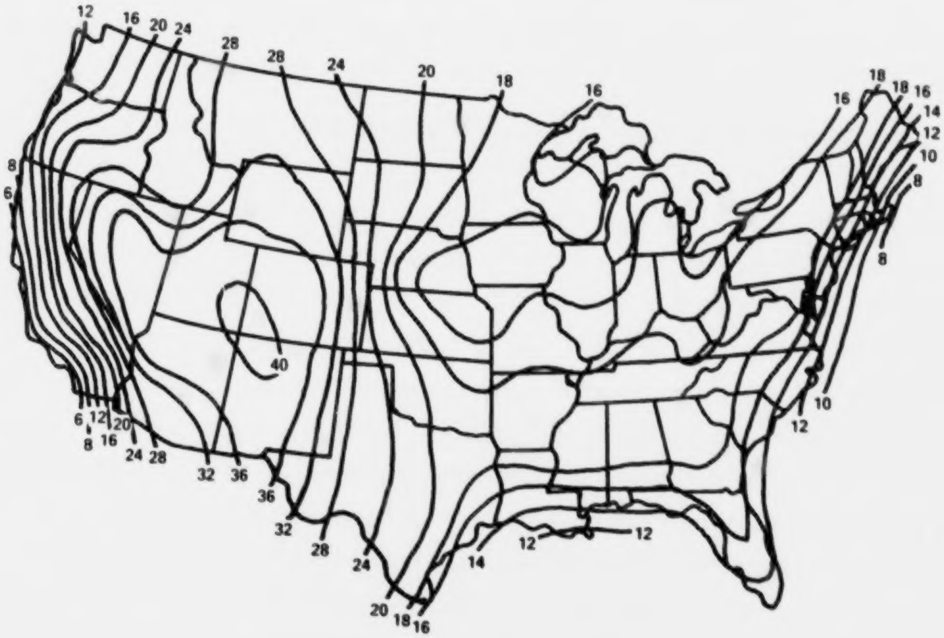
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Figure 3-5. Isopleths (m x 10^2) of mean summer afternoon mixing heights, AGL.

Source: Holzworth (1972).

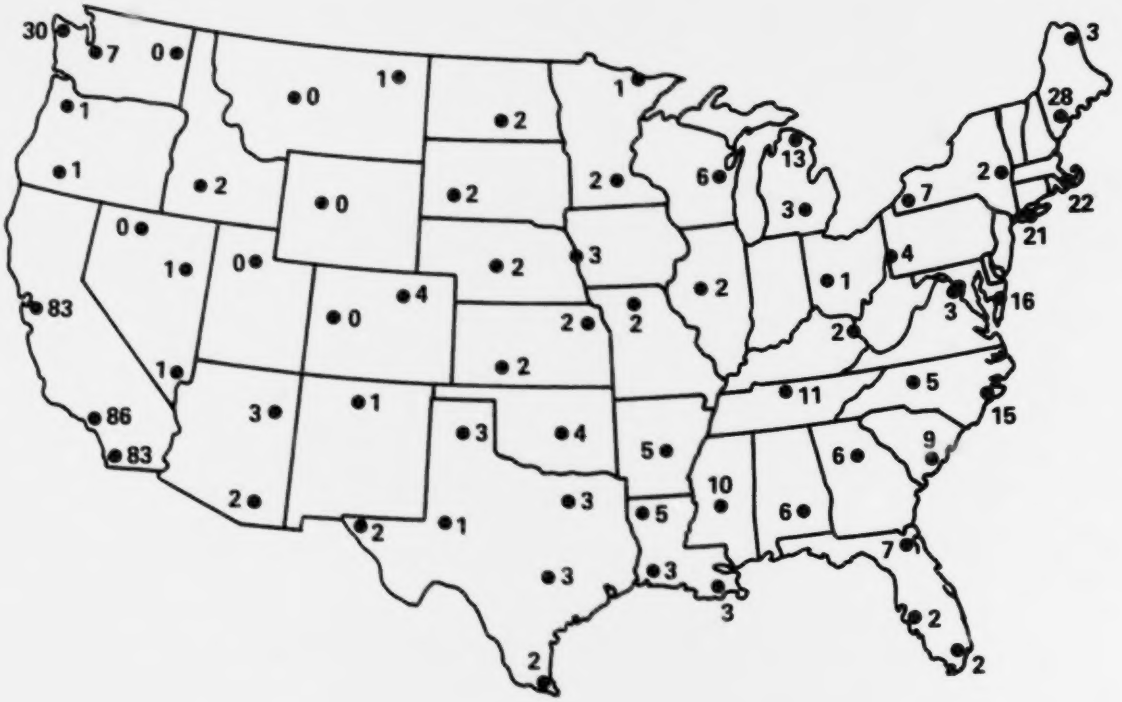


Figure 3-6. Percentage of summer 2315 GMT (6:15 p.m. EST, 3:15 p.m. PST) soundings with an elevated inversion base between 1 and 500 m above ground level.

Source: Adapted from Holzworth and Fisher (1979).

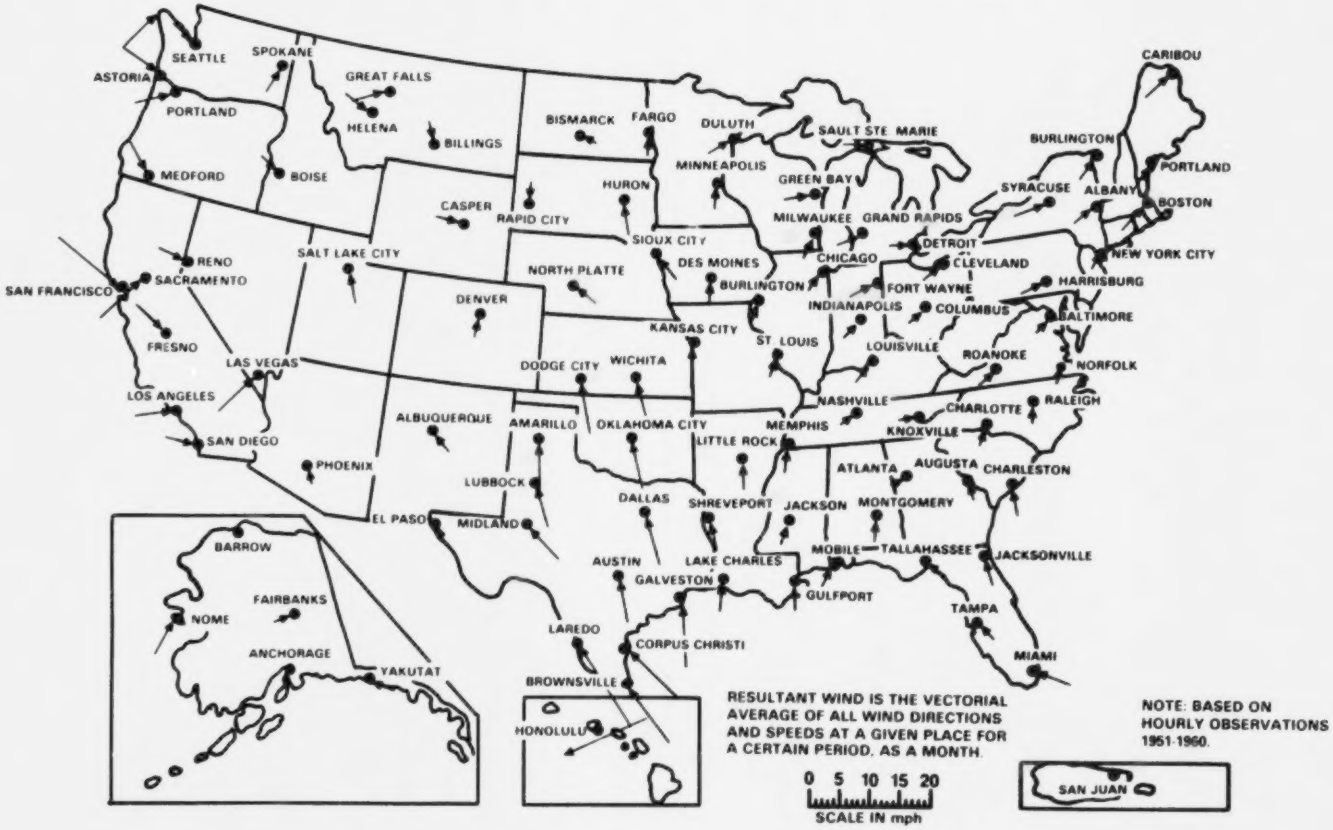
water prevails, also has a relatively high percentage, above 20 percent, compared to most of the rest of the country. Stations bordering one of the Great Lakes--Green Bay, Sault St. Marie, and Buffalo--reflect a stabilizing lake effect with percentages above 5 percent. Except along the Pacific Coast, these ocean and lake coastal situations are probably limited to relatively narrow coastal zones (Hosler, 1961). Examples are evident in Figure 3-6, in which it may be noted that inversion frequencies of 21 to 28 percent occur in coastal New England compared to only 2 percent at Albany in upstate New York. A similar situation is evident in a comparison of the 3 percent inversion frequency at Washington, D.C., with the 16 percent frequency on the Delaware coast. A non-coastal region having summer afternoon low-level elevated inversions more than 5 percent of the time is the Southeast, where an area from Louisiana and Arkansas to the Atlantic coast shows frequency values between 5 and 10 percent. Other seasons differ in details, but the general patterns are similar.

This means that, for most of the United States, low-level stable layers that persist through the afternoon hours are rare events, occurring on less than 1 day in 20. Thus, air pollution situations in areas such as Kansas or Iowa, although they can be the result of transport, may commonly be related to the periods when the expected morning surface inversion persists later in the morning than usual and when winds are not strong enough to carry pollutants rapidly away from the local area. Along both the Pacific Coast and the Northeast Coast, low-level afternoon inversions are frequent enough to be a significant contributor to local and regional air pollution episodes.

3.4.2 Wind Speed and Mixing

Another major meteorological factor in the urban pollutant dispersion problem is low-level or surface-layer wind. As would be expected, strong winds across a source area will dilute pollutant concentrations even though there is a strong, low-level inversion base. San Francisco is one example of such a location where strong winds frequently provide good ventilation in spite of a low inversion. Conversely, light and variable or calm wind conditions over an area can lead to excessive pollutant accumulations even though the afternoon mixing depth is quite large. Thus, it is necessary to include wind direction and wind speed frequencies in any evaluation of air pollution potential for a given area. It must also be recognized that both elevated inversion conditions and surface wind patterns are governed to a major degree by the synoptic, or large-scale, weather patterns. Both wind and inversion factors tend to favor pollutant buildup when a deep, slow-moving high-pressure system dominates the weather across an area (Korshover, 1967; Korshover, 1975).

Figure 3-7 shows the wind climatology across the United States in the month of July by depicting the monthly resultant vector wind at major weather stations (U.S. Department of Commerce, 1968). Note that the flow across the West Coast is generally directed inland, from west to east. This contributes to a typical situation for major California cities: significant urban pollutant plumes are found east of the urban core source areas while the immediate coastline or beach areas are relatively pollutant-free. In the Northeast States, the average wind flow is from southwest to northeast more or less parallel to the coastline. As a result, pollutant plumes from the major urban areas along this coast are frequently additive along the trajectory of the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RESULTANT WIND IS THE VECTORIAL AVERAGE OF ALL WIND DIRECTIONS AND SPEEDS AT A GIVEN PLACE FOR A CERTAIN PERIOD, AS A MONTH.

NOTE: BASED ON HOURLY OBSERVATIONS 1951-1960.

Figure 3-7. Mean resultant surface wind pattern for the United States for July. Direction and length of arrows indicate monthly resultant wind.

Source: U.S. Dept. of Commerce (1968).

wind. Polluted air moving toward the coast from major inland urban sources may also be a factor in this Northeast region. Along the Gulf Coast, the average winds form southerly, onshore flow. Under some weather situations, however, there is often an offshore flow in one area (e.g., Texas) and an onshore flow in an adjacent area. Thus, because of this recirculation, the onshore Gulf air masses are not always pollutant-free (Price, 1976; Wolff et al., 1981). Before the situation was examined carefully, the recirculating pollutants were sometimes confused with natural background concentrations.

Wind climatology provides an average wind flow pattern, but it does not provide a complete assessment of the influences of the wind on air pollution dispersion. Wind speed and, in particular, the frequency of weak winds are an important aspect to be considered. Figure 3-8, adapted from Holzworth and Fisher (1979), shows the frequency with which early morning (6:15 a.m. EST or 3:15 a.m. PST) surface inversions occur with calm or weak surface winds; that is, wind speeds equal to or less than 2.5 m/sec or 6 mi/hr. There is considerable variation between stations because terrain and geography (e.g., coastal locations) influence both the wind flow and inversion frequency. It is clear, however, that over large areas of the United States, especially in heavily industrialized inland areas east of the Mississippi River, calm amd stable summer mornings are a frequent occurrence: 50 percent or more in many areas. This means that there will be frequent incidents of morning pollutant accumulation; but afternoon heating, as shown by Figure 3-5, will usually mix the pollutant accumulations through a deep mixing layer and disperse them. Figure 3-9 (Holzworth and Fisher, 1979) shows the average wind speed through the depth of the summer morning mixing layer. Note that the area east of the Rocky Mountains, except for the Appalachians, can on the average, expect winds of 4 m/sec (about 10 mi/hr) or higher through the morning mixing layer. This probably would provide acceptable midmorning dilution of accumulated pollutants. In summer afternoons, as shown in Figure 3-10, the average wind speed within the mixing layer increases in all areas and may even double over some of the western mountain states. It should be noted, however, that since winds normally increase with altitude above the ground, much of the increase in the average afternoon mixing layer wind is probably the result of the considerable increase in the depth of the mixed layer, as shown by the differences between Figures 3-4 and 3-5.

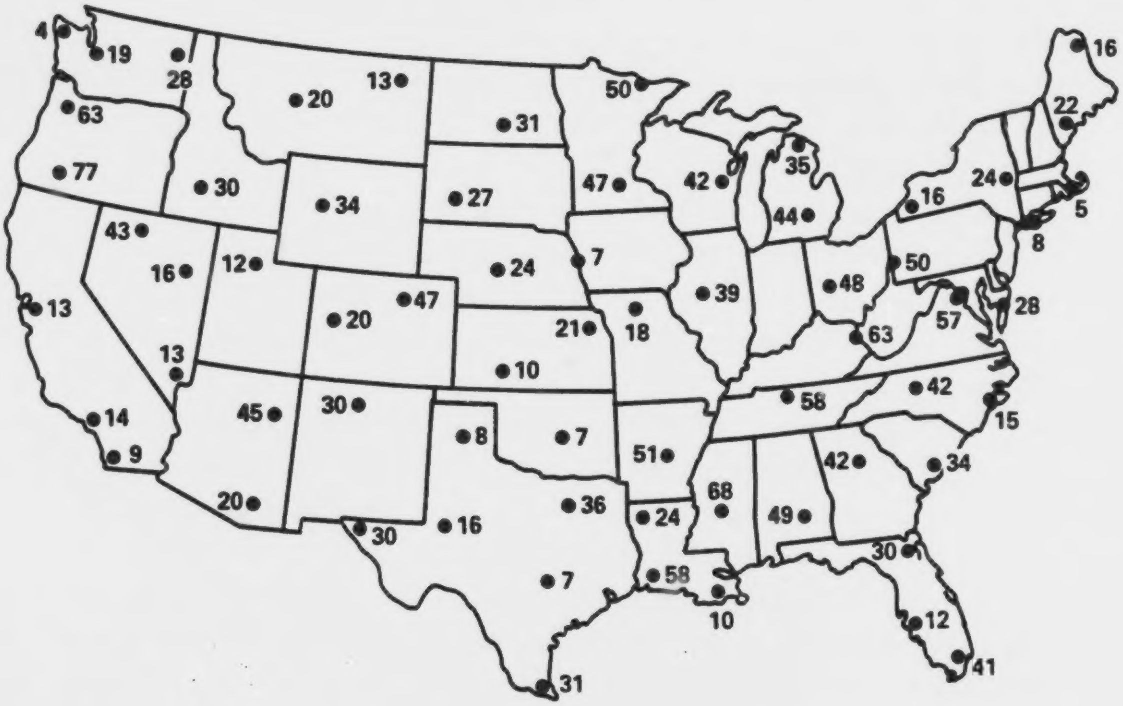
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Figure 3-8. Percentage of summer 1115 GMT (6:15 a.m. EST, 3:15 a.m. PST) soundings with an inversion base at the surface and wind speeds at the surface ≤2.5 m/sec.

Source: Adapted from Holzworth and Fisher (1979).

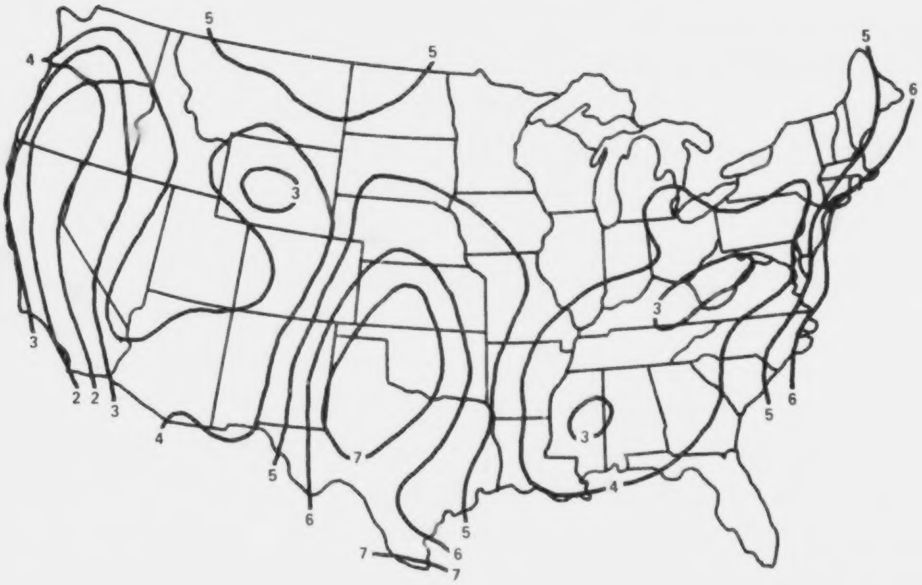
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Figure 3-9. Isopleths (m/sec) of mean summer wind speed averaged through the morning mixing layer.

Source: Holzworth and Fisher (1979).

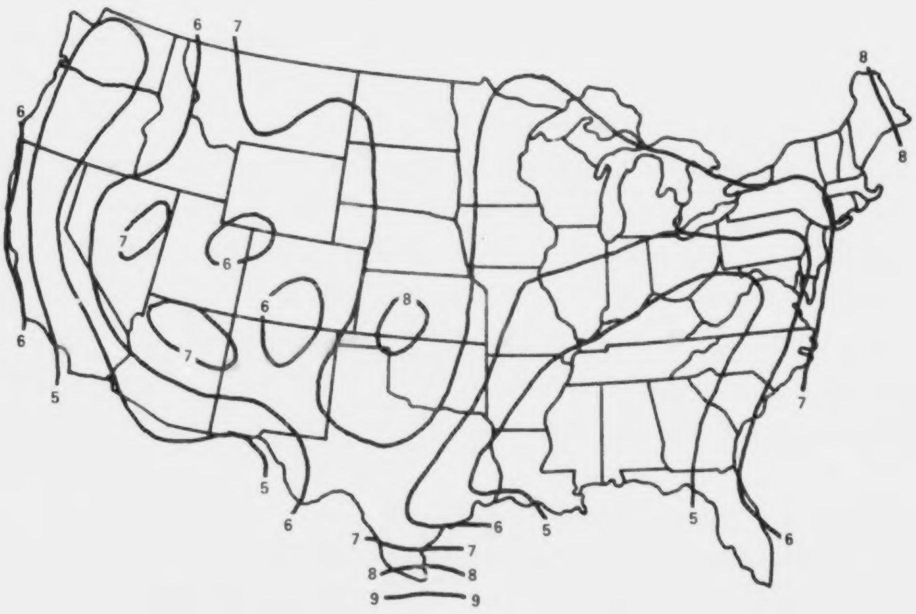
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Figure 3-10. Isopleths (m/sec) of mean summer wind speed averaged through the afternoon mixing layer.

Source: Holzworth and Fisher (1979).

In summary, atmospheric mixing parameters of stability and wind in the pollutant transport layers can exert controlling effects on O_3 and oxidant concentrations. The effects include the amount of dilution occurring in the source area, as well as along the trajectory followed by an urban or source-area plume. Regions having steady prevailing winds, such that a given air parcel can pass over a number of significant source areas, can develop significant levels of pollutants even in the absence of weather patterns that lead to the stagnation type of air pollution episodes. The Northeast states are highly susceptible to pollutant plume transport effects, although some notable stagnation episodes have also affected this area (e.g., Lynn et al., 1964). Along the Pacific Coast, especially along the coast of California, coastal winds and a persistent low inversion layer contribute to major pollutant buildups in urban source areas and downwind along the urban plume trajectory (Robinson, 1952; Neiburger et al., 1961). In the southern Appalachians, the weather favors longer-term air pollution episodes (Korshover, 1967; Korshover, 1975). Generally, low pollution potential results from the conditions that occur in the Great Plains area and south to the Texas-Louisiana Gulf Coast; and between the Mississippi River and the crest of the Rocky Mountains.

It should be clear even from this brief discussion that there are fundamental differences in regional meteorological conditions that cause the air pollution potential applicable generally to California to be more severe than in other parts of the United States. When adverse meteorology is coupled with high population and source concentrations, it is quite evident why California areas have severe photochemical air pollution problems. This very significant difference in the magnitude of the photochemical air pollution problem in California regions compared to non-California locations can serve as a basis for separating air pollution statistics into two sets for evaluation, namely, California and non-California groups.

3.4.3 Effects of Sunlight and Temperature

The significance of sunlight in photochemistry is related to its intensity and its spectral distribution, both of which have direct effects upon the specific chemical reaction steps that initiate and sustain oxidant formation. Sunlight intensity varies with season and geographical latitude but the latter effect is strong only during the winter months. During the summer, the maximum light intensity is fairly constant throughout the contiguous United States and only the duration of the solar day varies to a small degree with latitude.

The effects of light intensity on individual photolytic reaction steps and on the overall process of oxidant formation have been studied in the laboratory (Peterson, 1976; Demerjian et al., 1980). All of the early studies, however, employed constant light intensities, in contrast to the diurnally varying intensities that occur in the ambient atmosphere. More recently, the diurnal variation of light intensity has been recognized and studied as a factor in photochemical oxidant formation (Jeffries et al., 1975; Jeffries et al., 1976). Such studies showed that the effect of this factor varies with initial reactant concentrations. Most important was the observation that similar NMOC/NO_x systems showed different oxidant potential depending on whether studies of these were conducted using constant or diurnal light. This has led to incorporation of the effects of diurnal or variable light into photochemical models (Tilden and Seinfeld, 1982).

While the effect of sunlight intensity is direct and has been amply demonstrated (Leighton, 1961; Winer et al., 1979), the effect of wavelength distribution on the overall oxidant formation process is subtle. Experimental studies have shown the photolysis of aldehydes to be strongly dependent on radiation wavelength in the near UV region (Leighton, 1961); and there is some indication (Bass et al., 1980) that the photolysis rates for aldehydes may be temperature-dependent. Since aldehydes are major products in the atmospheric photooxidation of NMOC/NO_x mixtures, it is inferred that the radiation wavelength should have an effect on the overall photooxidation process. This inference was directly verified, at least for the propylene/NO_x and n-butane/NO_x chemical systems, in smog chamber studies (Jaffee et al., 1974; Winer et al., 1979). In the ambient atmosphere, some variation in the wavelength distribution of sunlight does occur as a result of variations in time of day, stratospheric O_3, ambient aerosol (Stair, 1961), and cloud cover.

It has been observed that days on which significant ozone-oxidant concentrations occur are usually days with warm, above-normal temperatures (Bach, 1975). The possibility that photochemical reactions show some temperature dependence has been raised by smog chamber studies (e.g., Carter et al., 1979; Countess et al., 1981), but is usually thought to be the production of chamber artifacts concomitant with increases in temperature. In ambient air, the observed correlation between temperature and oxidant concentrations can be explained, at least in part, as a synoptic meteorological correlation rather than as a temperature-photochemical rate constant effect, in that periods of clear skies and warm temperatures are periods of high air pollution potential, as discussed above. Because of the close correlation between above-normal temperatures and high photochemical air pollution potential, a maximum daily temperature forecasting procedure is often useful as a substitute for a more elaborate and specific program for forecasting possible photochemical air pollution. The correlation between temperature and, thus, synoptic weather conditions and photochemical air pollution intensity has been observed in a number of areas. Evaluation of photochemical air pollution in Los Angeles as early as 1948 showed a correlation with temperature. Recent studies of O_3 patterns in St. Louis, Missouri, have also shown a correspondence between daily maximum O_3 concentration and temperature (Shreffler and Evans, 1982). Wolff and Lioy (1978) have shown high correlations between ozone concentration and both the temperature for the current day and the temperature for the previous day.

3.4.4 Transport of Ozone and Other Oxidants and Their Precursors

The 1978 air quality criteria document for ozone and photochemical oxidants made a convincing case for the fact that ozone and other photochemical oxidants are transported from urban source areas, other than those in California, to downwind regions in concentrations of 0.1 ppm or greater (U.S. Environmental Protection Agency, 1978a, and references therein). The 1972 study by Research Triangle Institute at McHenry, Maryland, was an early examination of rural oxidant in the eastern United States (Ripperton et al., 1977). Bach (1975) examined the meteorology of these observed conditions and showed details of the influence of transient high pressure systems. The transport of large urban plumes in the northeastern states, especially from New York City into Connecticut, was the subject of an EPA field study in 1975 (Westberg et al., 1976; Wolff et al., 1977d; Westberg et al., 1978a). Transport of ozone on a regional basis in the northeast was also described by Cleveland et al. (1976a, 1976b), while Wolff et al. (1977a) presented details of several east coast urban oxidant plumes. The Northeast Regional Oxidant Study (NEROS) carried out by EPA in 1979 and 1980 in the corridor from Washington, D.C., to Boston, was designed specifically to support urban plume model development (Clarke et al., 1982). Plume models have been based on other urban plume investigations, as well (e.g., Wolff et al., 1977c), and reactive plume modeling for other urban areas has progressed in recent years (e.g., U.S. Environmental Protection

Agency, 1981a). These several early research programs and analyses served to answer a number of perplexing problems that had been identified previously in studies of ozone and other photochemical oxidants in nonurban areas (e.g., Ripperton et al., 1977; Bach, 1975). These questions included reasons for the occurrence of high ozone or total oxidant concentrations in areas remote from identifiable sources.

Studies of the transport of ozone and other photochemical oxidants (O_3-O_x) are classified into three regimes, depending upon transport distance (U.S. Environmental Protection Agency, 1978a). In the first, urban-scale transport, the occurrence of transport of photochemical pollutants can be detected in most large urban areas if there is sufficient O_3-O_x monitoring information. It has been identified as a significant, characteristic feature of the O_3-O_x problem in the Los Angeles basin (Tiao et al., 1975), as well as in San Francisco, New York, Houston, Phoenix, and St. Louis (Altshuller, 1975; Coffey and Stasiuk, 1975; Shreffler and Evans, 1982; Wolff et al., 1977a). As noted above, the recognition and assessment of the probable magnitude of urban oxidant problems in locations other than in California has been a major research topic since the mid-1970s (e.g., Bach, 1975; Cleveland et al., 1976a, 1976b; Westberg et al., 1976; Wolff et al., 1977a,b,c; and others).

Urban-scale transport patterns result from one or more of a combination of factors. First is the simple advection of the photochemically reacting air mass and the development of maximum O_3-O_x after 1 or 2 hours of downwind travel. Maximum concentrations may be displaced up to 20 or so miles from the center of the major source area. It has been noted (U.S. Environmental Protection Agency, 1978a) that pollutant concentrations in air parcels in the central core area of major source areas may not be the most conducive for O_3-O_x formation because of the tendency toward occurrence there of more effective scavenging, especially scavenging related to NO and its reactions.

The distance of the peak O_3-O_x concentrations from the urban core area is dependent on the local wind pattern and is, in general, inversely related to the peak O_3-O_x concentration. Stronger winds will carry the air parcels farther during the reaction period, increasingly diluting pollutant concentrations along the trajectory. Weak winds and very restricted mixing heights will tend to cause higher O_3-O_x concentrations closer to the central source area. The diurnal wind cycle will also be an important factor, since in some situations calm conditions may prevail until late in the morning but in others a steady wind may be present throughout the emission and reaction process. Wolff and Lioy (1978) were able to model urban ozone concentrations on the basis of meteorological observations, especially temperature.

The second, or mesoscale, kind of transport of O_3-O_x is in many respects an extension of the urban-scale transport and is characterized by urban plume development. A report by Bell (1960) described November 1959 O_3-O_x incidents in northern coastal San Diego County, California. It showed conclusively that these were caused by the O_3-O_x and precursors formed and emitted, respectively, the previous day in the Los Angeles basin. The transport in these situations was over the coastal Pacific Ocean, and the O_3-O_x arrived at the San Diego receptor site as a contaminated sea breeze after overnight travel (Bell, 1960). The studies of Cleveland et al. (1976a, 1976b) are early documentation of a similar scale of transport in the New York-Connecticut area. The results of extensive aircraft measurements and modeling assessments of studies in the Washington, D.C., to Boston corridor have also been reported by Wolff and his colleagues (Wolff et al., 1977a,c; Wolff and Lioy, 1978).

In the 1978 O_3-O_x criteria document, more than 30 references were cited relating to urban plume observations and investigations. Since that document was published, the results of the 1975 New England oxidant study have been published in detail (e.g., U.S. Environmental Protection Agency, 1977; Westberg et al., 1978a), and results of a more comprehensive 2-year field program carried out along the Washington, D.C.-Boston corridor in 1979 and 1980 have appeared in the literature (Clark and Clarke, 1982; Clarke et al., 1982; Vaughan et al., 1982). A major field program supported by local industries has been conducted in Houston, Texas, although the O_3-O_x downwind plume phases of that study were not as extensive as in NEROS. Chicago, Detroit, and adjacent shoreline areas of Lake Michigan have also been the subject of a number of ground-level and airborne studies over distances of 70 to 300 kilometers (Lyons and Olsson, 1972; Sexton and Westberg, 1980; Westberg et al., 1981; Kelly et al., 1986). As described above, O_3-O_x plumes from major urban areas can extend about 100 to 200 miles, with widths of tens of miles (Sexton, 1982), frequently up to half the length of the plume. Other field studies conclusively demonstrating mesoscale transport over New England have been reported (Spicer et al., 1979; Clarke et al., 1982; Cleveland et al., 1976a,b; Rubino et al., 1976; Westberg et al., 1976; Westberg et al., 1978a; Wolff et al., 1977a). Although urban plumes are frequently thought of as a problem related only to large source areas such as New York and other major metropolitan areas, measurements in plumes from smaller urban areas have shown that these sources cannot be ignored (Sticksel et al., 1979; Sexton, 1982; Spicer et al., 1982; Wolff et al., 1977c).

In the third kind of pollutant transport, synoptic-scale, the transport of O_3-O_x and precursors is characterized by the general and widespread elevated concentrations of pollutants that can occur on an air-mass scale under certain favorable weather patterns. These weather situations are generally slow-moving, well-developed high-pressure, or anticyclonic systems. This type of deep high-pressure area was considered by Korshover (1967, 1975) as a prerequisite for stagnating air pollution episodes.

A major criterion of these synoptic systems is the reinforcement of the surface high-pressure area by a warm high-pressure circulation in the upper air. The surface weather is then frequently characterized by weak winds, stable surface layers, and high pollution potential over regional or air-mass-sized areas. This is the generalized meteorological model pattern that is involved in synoptic-scale pollutant transport (Korshover, 1967; Korshover, 1975). As with all generalized models, there have been specific oxidant episodes that departed from this model. In particular, weak winds are not always a prerequisite; and relatively strong winds have been observed to be associated with some oxidant transport episodes (Mueller and Hidy, 1983; Wolff and Lioy, 1980), when such winds did not also produce rapid plume dilution as is usually expected.

While surface highs that are reinforced aloft by a warm high can lead to air pollution episodes, there are other high-pressure systems that usually cause few or no widespread air pollution problems. These are the strong surface highs found behind rapidly moving storm systems, in which the surface high underlies a cold low-pressure system aloft. These systems characteristically have good vertical mixing (instability), brisk winds, and low air pollution potential.

Bach (1975) assessed in detail the relationship between elevated ozone levels and synoptic systems. Other investigators have since described specific instances of large-scale ozone transport and associated meteorological conditions (e.g., Wolff and Lioy, 1980; Wolff et al., 1980; Wolff et al., 1982). For example, Wolff et al. (1982) have described synoptic meteorological systems and the occurrence of haze and elevated ozone levels in an area extending from the Midwest to the Gulf Coast. In a separate study, Wolff and Lioy (1980) examined the spatial and temporal distributions of ozone during three photochemical smog episodes in July 1977. A stagnating high-pressure system formed over the Gulf of Mexico and two high-pressure systems originating in Canada were described as the respective meteorological systems associated with the three episodes. In all three cases, elevated ozone concentrations (~120 to 130 ppb) were found to extend, in a virtual "ozone river", from the Gulf Coast to New England (with 328 ppb ozone measured in Connecticut). The high-pressure system originating in the Gulf area affected the entire southeastern United States and extended from western Texas, northeastward through Illinois, and east to the Atlantic Ocean. Elevated ozone levels affected anywhere from a few hundred square miles to a thousand square miles during the 1-week period.

The importance of synoptic-scale or air-mass pollutant situations has been recognized for many years, probably much longer than the importance of major plumes has been apparent. The Donora, Pennsylvania, smog episode in 1948 (Schrenk et al., 1949), while not a photochemical smog situation, involved the occurrence over a wide area of a regional air mass having relatively high pollution levels simultaneous with the occurrence of a stagnating warm high-pressure area over the Ohio Valley and the northern Appalachian area. Donora was an especially adversely affected pocket within this larger system; in that case, however, ozone was probably not one of the important pollutants.

The synoptic-scale high-pressure air pollution system is not characterized by well-defined urban plumes. Rather, a warm, slow-moving or stagnant anti-cyclone provides a synoptic-scale weather system that, because of weak winds and limited vertical mixing, favors the accumulation of relatively high concentrations of air pollutants. On a climatological basis, these systems are most common in the summer and fall months over most of the United States, as shown by the work of Korshover (1967; 1975). In many cases, an anti-cyclone will stagnate or recurve and intensify over the Midwest or East as circulation patterns in the upper air change and become more supportive of the surface anti-cyclonic pattern (Schrenk et al., 1949; Lynn et al., 1964). The typical paths followed by the air masses forming these slower-moving anticyclones in the summer and fall months, as described by Bach (1975) and Wight et al. (1978), is southeastward from Canada into the upper Mississippi Valley, eastward across the Ohio Valley and then across the East Coast, either toward the northeast into New England, east into the central Atlantic States, or southeast into the southeastern states. The actual stagnation of a pressure system for one or more days, as occurred in the Donora case, is, of course, the most severe example of a slow-moving system.

Along the West Coast, air pollution problems are also the result of persistent high-pressure system influences. In this case, however, the high is the persistent subtropical anti-cyclone of the eastern Pacific rather than the series of transitory anti-cyclonic systems characteristic of the area east of the Rocky Mountains. The persistent or semipermanent subtropical anti-cyclone in the Pacific is linked to the large-scale general circulation of the atmosphere rather than to moving wave systems (Neiburger et al., 1961). The effect is much the same, except that the area of limited mixing and more adverse air pollutant effects is found on the eastern edge of the subtropical anti-cyclone rather than on the trailing western edge as in the transitory systems.

It is worthwhile to point out that the typical pattern of ozone concentrations in the slow-moving midwest anticyclone, in contrast to the conditions in California, shows the lowest values in the eastern portion of the system, behind the advancing cold front. The central area of the anticyclonic system, where dispersion is usually at a minimum, shows a broad expanse of elevated ozone concentrations; but the highest ozone values in the typical system are usually found in the western parts of the system, the so-called "back side," where dispersion conditions, although better than in the central portion of the system, combine with increased residence time and longer exposure to emission sources to cause the maximum ozone concentrations in a given high-pressure system. Investigators describing this ozone pattern over the midwestern and eastern parts of the United States include Bach (1975), Vukovich et al. (1977), Wolff et al. (1977b), Wight et al. (1978), and Westberg et al. (1978a, 1981).

The identification and understanding of photochemical O_3-O_x and precursor transport by weather systems has provided a significant advance in comprehending photochemical air pollution and the potential extent of its effects. Considerable progress has been made in the development of long-range photochemical modeling techniques so that the likely impact of synoptic systems can be anticipated. Such tools are very much in the research stage because the local impact of O_3-O_x results from a complex interaction of distant and local precursor sources, urban plumes, mixing processes, atmospheric chemical reactions, and general meteorology.

3.4.5 Surface Scavenging in Relation to Transport

Major scavenging processes for O_3 in the atmospheric boundary layer are adsorption and subsequent destruction at the ground surface (i.e., dry deposition), and reactions with boundary layer pollutants, especially NO and alkenes. In dry deposition, eddy diffusion moves air parcels downward through the turbulent boundary layer to the laminar sub-layer where individual molecules, such as ozone, can move by Brownian motion to the underlying surface. There reactive molecules, such as ozone, can be removed by reactions at the surface. Chemical reactions between ozone and NO and reactive hydrocarbons are described in other sections of this document. When they occur in the near-surface layers, these reactions can play an important role in the boundary layer scavenging process. Dry deposition and boundary layer chemical reactions result in a vertical concentration gradient, with the lowest concentrations occurring at the surface of the ground.

Because of this surface-scavenging process, ozone will persist in an atmospheric parcel in the absence of ozone-forming reactions only if the parcel is dispersed such that contacts with the ground surface or surface pollutant sources are minimized. It is likely that only in those air parcels moving above the surface layer will ozone escape the surface reactions and persist long enough to undergo long-distance transport or persist overnight. It should be noted here that ozone transported aloft, judging from the limited data available, may be 20 to 70 percent additive in urban areas, as determined by simulations using the EKMA chemical kinetics model and several different rates of vertical mixing (U.S. Environmental Protection Agency, 1977b). Thus, if 0.1 ppm ozone were to be transported aloft and was 40 percent additive at ground level, the contribution of transport to the peak ozone concentration downwind would be 0.04 ppm.

Aircraft observations have documented frequently the occurrence of relatively high ozone concentrations above lower-concentration surface layers (e.g., Westberg et al., 1976). This is a clear indication that ozone is essentially preserved in layers above the surface and can be transported over relatively long distances even when continual replenishment through precursor reactions is not a factor, such as at night. Boundary-layer scavenging processes are also responsible for the fact that ozone concentrations in urban areas rapidly fall to zero during the night.

3.4.6 Stratospheric-Tropospheric Ozone Exchange

The fact that O_3 is formed in the stratosphere, mixed downward, and incorporated into the troposphere, where it forms a more or less uniformly mixed background concentration, has been known in various degrees of detail for many years (Junge, 1963).

It is widely accepted that the long-term average tropospheric background concentration at the surface ranges from about 30 ppb to 50 ppb (Fabian and Pruchniewicz, 1977; Oltmans, 1981); and that it results primarily, though not exclusively, from the transfer of stratospheric ozone into the upper troposphere, followed by subsequent dispersion throughout the troposphere (e.g., Singh et al., 1980; Kelly et al., 1982). Ozone residence time in the troposphere has been estimated at 1 to 2 months by Junge (1963); and at 1 to 2 months for spring and summer but at 2.5 to 3.5 months for fall and winter, respectively, by Singh et al. (1980).

The mechanisms by which stratospheric air is mixed into the troposphere have been examined by a number of authors. Danielsen conducted extensive analyses of major synoptic weather events that injected stratospheric air into the troposphere (Danielsen, 1968; Danielsen and Mohnen, 1977; Danielsen, 1980). Reiter has been especially active in describing the atmospheric mechanisms by which stratospheric air injection takes place and in relating these processes to the global circulation of the atmosphere (Reiter, 1963; Reiter and Mahlman, 1965; Reiter, 1975). As a result of such research, exchange between the stratosphere and troposphere in the middle latitudes has been determined to occur to a major extent in events called "tropopause folds." In a tropopause fold (TF), the jet stream in the upper troposphere plays a major role in directing stratospheric air and high ozone concentrations into the troposphere. Figure 3-11 is a schematic presentation of the intrusion process as described by Danielsen (1968). The subsidence occurs along the poleward side of the polar jet stream in the area where the jet is associated with a cold front at ground level. The result is downward transport in the cold air behind the cold front.

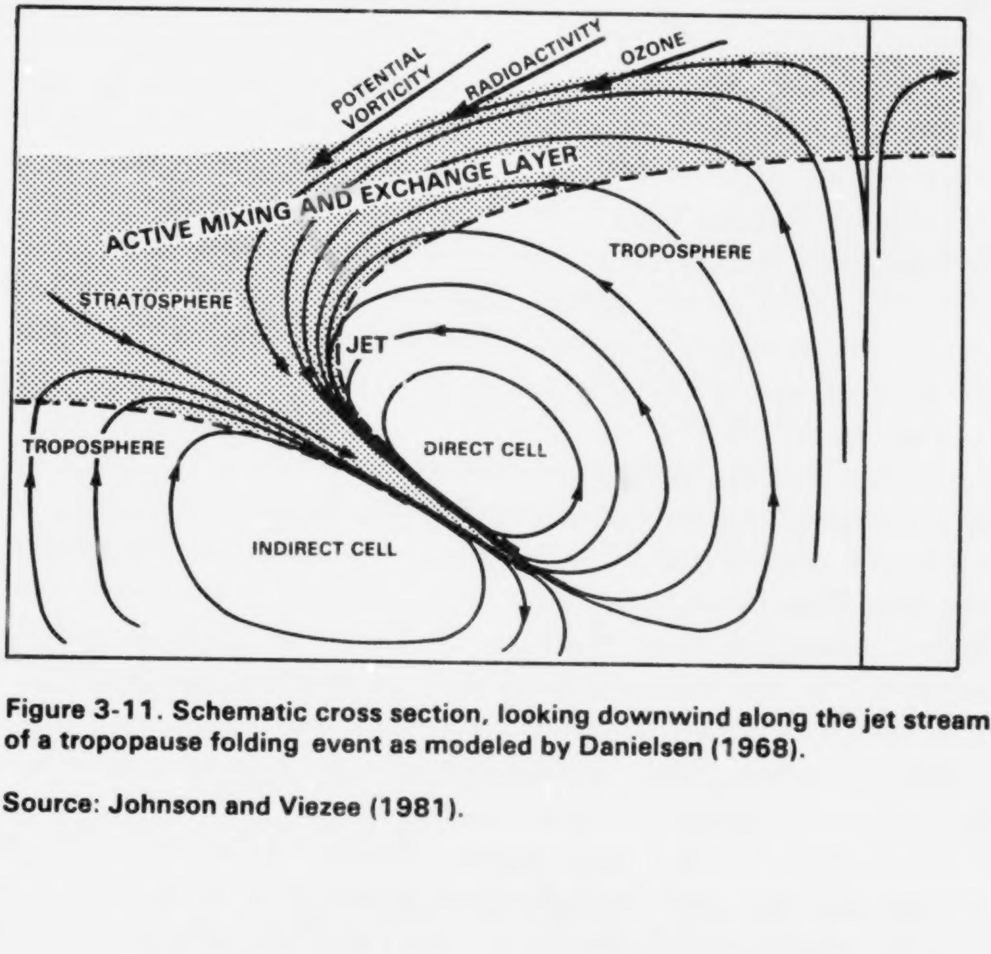

POTENTIAL VORTICITY
RADIOACTIVITY
OZONE
ACTIVE MIXING AND EXCHANGE LAYER
STRATOSPHERE
TROPOSPHERE
JET
DIRECT CELL
TROPOSPHERE
INDIRECT CELL

Figure 3-11. Schematic cross section, looking downwind along the jet stream, of a tropopause folding event as modeled by Danielsen (1968).

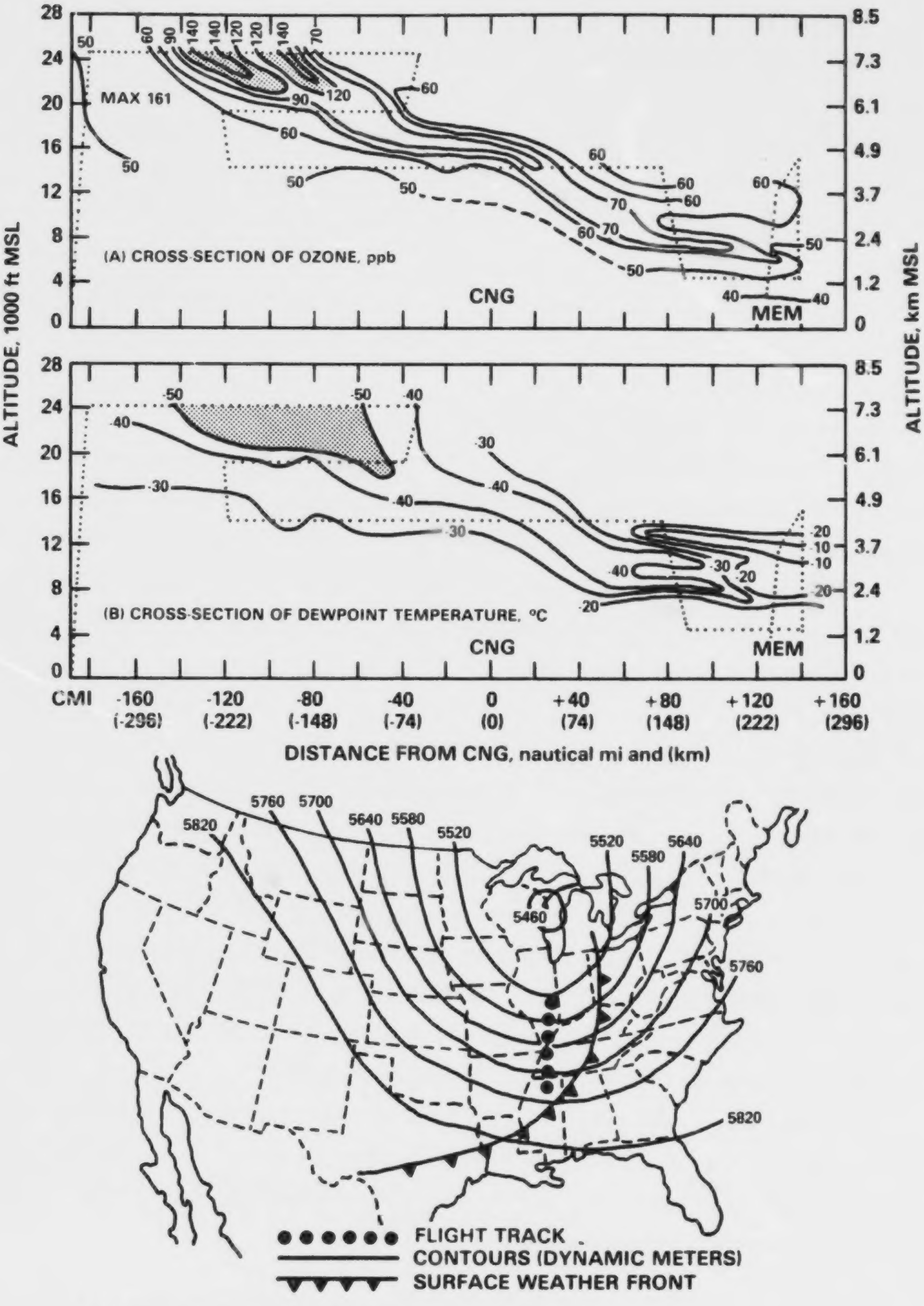
Source: Johnson and Viezee (1981).

Since 1978, a considerable amount of research on TF and ozone injection has been done, especially by SRI-International (Johnson and Viezee, 1981; Ludwig et al., 1977; Singh et al., 1980; and Viezee et al., 1979). Figure 3-12 from Johnson and Viezee (1981) shows one example of the probing by SRI of a TF event in the midwestern United States. Concentrations of ozone in excess of 90 ppb were found as low as 13,000 feet (ca. 2.5 miles or 3.9 kilometers), as shown in the upper part of Figure 3-12. These authors found that ozone intrusion was lower during this fall study (October 5, 1978) than in a number of other spring TF events. The dew point measurements in the second part of the figure confirm the stratospheric injection. The weather pattern accompanying this TF is shown at the bottom of Figure 3-12 by a 500 millibar (about 6 kilometer) chart; the surface cold front is also indicated. Note that the intrusion was detected well behind the cold front and appears to have assumed a layered formation in the altitude range of 8,000 to 12,000 feet (2.4 to 3.6 kilometers).

From their analysis of measurement flights in a number of TF situations, Johnson and Viezee (1981) concluded that the ozone-rich intrusions studied sloped downward toward the south. In terms of dimensions, the average crosswind width (north to south) at an altitude of 5.5 kilometers (ca. 18,000 feet or 3.4 miles) for six spring intrusions averaged 226 kilometers (364 miles), and for four fall TF systems, 129 kilometers (208 miles). Ozone concentrations at 5.5 kilometers (ca. 18,000 feet or 3.4 miles) averaged 108 ppb in the spring systems and 83 ppb in the fall systems. Previously it had been assumed that only a few fairly intense systems would produce a TF event and trans-tropopause mixing. From their data, however, Johnson and Viezee (1981) drew the very important conclusion that all low-pressure trough systems, such as that illustrated in Figure 3-12, may induce a TF event and cause the trans-tropopause movement of ozone-rich air into the troposphere.

On the basis of their field studies and the earlier models and work of Danielsen (1968), Johnson and Viezee (1981) proposed a set of model mechanisms or types of TF injection, which are illustrated in Figure 3-13 and described in the following general manner:

1. Type 1. The intrusion is broken up and dispersed by mixing and diffusion in the middle or free troposphere.
2. Type 2. The intrusion persists down to the planetary boundary layer or the top of the mixed layer, where the lower part of the intrusion may be incorporated into the mixed layer and may subsequently reach the ground.



(C) 500-mb CHART AND FLIGHT TRACK

Figure 3-12. Measured vertical cross-sections of (A) ozone, (B) dew-point, and (C) the 500-mb chart and the flight track for October 5, 1978. CMI = Champaign, IL; CNG = Cunningham, KS; MEM = Memphis, TN.

Source: Johnson and Viezee (1981).

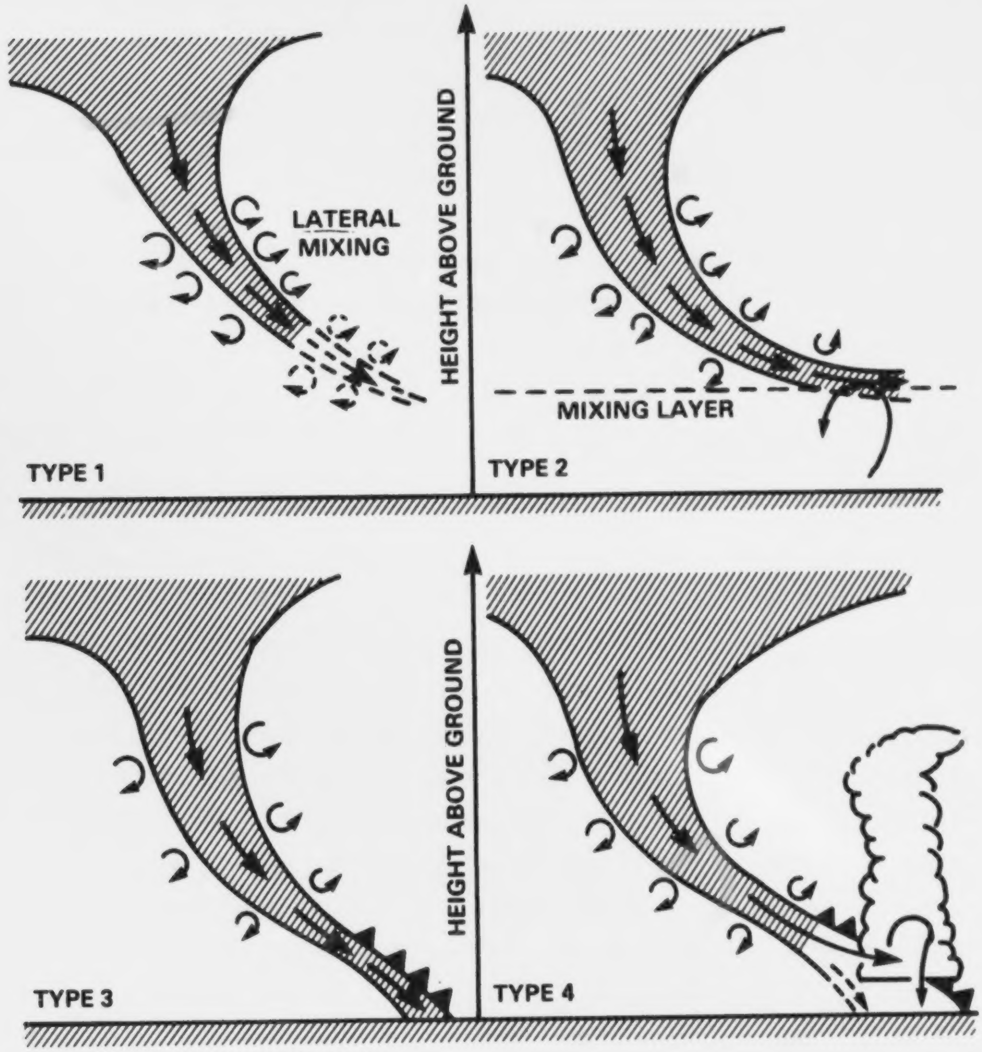

LATERAL MIXING
HEIGHT ABOVE GROUND
MIXING LAYER
TYPE 1
TYPE 2
HEIGHT ABOVE GROUND
TYPE 3
TYPE 4

Figure 3-13. Hypothesized models of the process that mixes tropopause folding events into the troposphere.

Source: Johnson and Viezee (1981).

3. Type 3. The intrusion occurs close behind the cold front, where the air parcels are caught by the downdrafts behind the cold front; and is brought to the ground by direct circulations associated with the front.

4. Type 4. The ozone-rich parcels are incorporated into convective cells and brought to the ground in association with rain-showers and thunderstorm downdrafts; similar to Type 3.

Johnson and Viezee (1981) summarized the possible impacts of these four types of TF events by noting that Types 1 and 2 should produce "relatively moderate effects" at the ground in comparison to those to be expected from Types 3 and 4. The latter two could cause "substantial" effects in terms of high surface ozone concentrations. The action described by Types 3 and 4 is supported by meteorological theory (Bjerknes, 1951) and by observations of surface ozone such as those made by Danielsen and Mohnen (1977), Lamb (1977), and Davis and Jensen (1976).

3.4.7 Stratospheric Ozone at Ground Level

After a detailed review of background tropospheric ozone, Viezee and Singh (1982) concluded, as also concluded by other investigators (e.g., Kelly et al., 1982), that the stratosphere is a major but not the sole source of background ozone in the unpolluted troposphere. This stratospheric ozone is brought to the surface mixed layer by vertical mixing processes that have been known for many years (Junge, 1963). In the northern hemisphere, at midlatitudes between 30°N and 50°N, annual average background surface ozone concentrations generally range between 30 and 50 ppb, but in the tropics, lower concentrations, 15 to 20 ppb, prevail (e.g., Fabian and Pruchniewicz, 1977; Oltmans, 1981). The stratospheric ozone reservoir has a strong seasonal variation, with a maximum in the spring and a minimum in fall and winter months, especially at middle latitudes. This seasonal cycle is reflected at ground-level background observation stations, where the average spring background ozone at some stations may be as high as 80 ppb and the average fall values range between 20 and 40 ppb (e.g., Singh et al., 1977; Mohnen, 1977; U.S. Environmental Protection Agency, 1978). In the troposphere, concentrations generally increase gradually to the tropopause, but the seasonal pattern is the same (Viezee and Singh, 1982).

Using data acquired in their studies of TF events, researchers at SRI-International examined the frequency with which stratospheric intrusions occur.

According to Singh et al. (1980), an intrusion can be expected to be present over the United States on about 90 percent of the days. This frequency diminishes somewhat in summer, however (Singh et al., 1980), which is the season when most ground-level smog episodes occur.

Viezee and Singh (1982) concluded that relatively high ozone concentrations can occur for short periods of time, minutes to a few hours, over local areas as a result of stratospheric intrusions. They were able to document from published literature ten situations of probable intrusion of stratospheric ozone. These instances are shown in Table 3-7, reproduced from Viezee et al. (1983). The concentrations reported in Table 3-7 were measured at ground-level stations. Note that all of the short-term situations in which peak concentrations exceeded 80 ppb occurred in fall, winter, or spring months and not in the photochemically active summer season. Of the three summer instances that were reported, two at Whiteface Mountain, New York, and one at Pierre, South Dakota, the highest reported concentration was 56 ppb for a 1-hr average. The lower incidence in summer of reported ground-level impact by stratospheric ozone may be attributable in part to the reduced frequency of intrusions in summer, as reported by Singh et al. (1980). In addition, however, the potential for ground-level impact by stratospheric ozone in summer is lessened because of the stability provided by the upper-level, warm anticyclone present in the weather systems characteristic of summertime photochemical smog episodes.

There have been a number of attempts to quantify the proportion of the surface ozone attributable to stratospheric sources. The most common method used is based on the assumption that ^{7}Be is a unique tracer for air parcels of stratospheric origin. Both ozone and ^{7}Be are measured and the proportion of the surface ozone that might be of stratospheric origin is calculated by using a derived ratio between ozone and ^{7}Be. Some of the investigators using this technique include Ferman and Monson (1978), Wolff et al. (1979), Husain et al. (1977), Dutkiewicz and Husain (1979), Singh et al. (1980), and Johnson and Viezee (1981), among others.

Calculated correlations between surface ozone and ^{7}Be show that their relationship is variable. The results of Kelly et al. (1982), from studies of ^{7}Be, O_3, and air mass classification in South Dakota, showed that continental tropical (cT) air masses frequently seemed to have higher ^{7}Be and O_3 values on the western side of the traveling cT anticyclone. A similar relationship was not prominent in the polar air masses studied, however, and maritime tropical

TABLE 3-7. PUBLISHED EPISODES OF TRANSPORT OF STRATOSPHERIC OZONE TO GROUND LEVEL

Case no.	Date	Geographic location	Ground-level O_3 concentration, ppb	Duration of observed event	Length of data record examined	Source
1	3 March 1964	Quincy, Florida (near Tallahassee)	100 to 300	3 hr	July 1963 through July 1973	Davis and Jensen (1976)
2	26 February 1971	Observatory Hohenpeissenberg (1000 m MSL), SW of Munich, Germany	415 250	10 min 50 min	December 1970 through May 1971	Atmannspacher and Hartmannsgruber (1973)
3	19 November 1972	Santa Rosa, California	200 to 230	1 hr	November 1972	Lamb (1977)
4	6 March 1974	Harwell, Oxon, United Kingdom	110 to 115	2 hr	4 to 5 yr discontinuous	Derwent et al. (1978)
5	8,9 January 1975	Zugspitze Mountain, near Garmisch-Partenkirchen, Germany (3000 m MSL)	160 to 193	4 hr	August 1973 through February 1976	Singh et al. (1980)
9	11, 12 July 1975	Whiteface Mountain, New York (1150 m MSL)	$\leq$ 37	24-hr average	July 1975	Husain et al. (1977)
4	19 March 1977	Sibton, Suffolk, United Kingdom	100 to 110	2 hr	4 to 5 yr discontinuous	Derwent et al. (1978)
10	24, 25, 28 June and 1 July 1977	Whiteface Mountain, New York	$\leq$ 47	24-hr average	June and July 1977	Dutkiewicz and Husain (1979)
6	4 March 1978	Denver, Colorado	82	1 hr	1975 to 1978	Haagenson et al. (1981)
7	July 1978	Pierre, South Dakota	$\leq$ 56 $\leq$ 46	1 hr 24-hr average	July through September 1978	Kelly et al. (1982)
8	15 March 1978	Kisatchie National Forest, Louisiana	100 to 105	2 hr	Spring 1978	Viezee et al. (1982)

Source: Viezee et al. (1983).

air masses did not reach the South Dakota site. Kelly et al. (1982) found a linear correlation, r, equal to 0.65, for 1978 summer measurements of ^{7}Be and ozone in South Dakota. Ferman and Monson (1978) reported r = 0.60 at McKee, Kentucky, for 27 daily samples taken during August and September 1976. Johnson and Viezee (1981) reported an r value of about 0.50 for ^{7}Be and ozone data from Dodge City, Kansas, during April and May 1978. A much lower correlation, r = 0.15, was reported by Husain et al. (1977) for July and August 1975 measurements at Whiteface Mountain, New York. These data imply that the variability of the surface ozone concentration that can be explained by ^{7}Be varies from about 40 percent to less than 5 percent.

Singh et al. (1980) and Viezee and Singh (1982) have pointed out a number of problems with this technique in their detailed analyses of the application of ^{7}Be measurements to the quantification of the amount of stratospheric ozone in surface air. Some of the problems encountered when applying ^{7}Be/O_3 ratios over short sampling periods (in contrast, for example, to seasonal averages) include the following:

1. Because ^{7}Be is an aerosol and O_3 is a gas, they have fundamentally different atmospheric scavenging mechanisms and thus respond differently to tropospheric meteorological conditions.
2. Although the stratosphere is its dominant source, on the average, ^{7}Be is synthesized in both the troposphere and the stratosphere. The ^{7}Be source cannot be assumed to be equivalent to the O_3 source without meteorological verification.
3. ^{7}Be sampling data are primarily averaged over 24 hours, which does not give sufficient time resolution for disaggregating short-period, rapidly moving stratospheric intrusion events from longer-term processes.
4. The lower stratosphere is a highly variable and poorly characterized region for which no ^{7}Be/O_3 ratio has been firmly established.

As a result of these and other factors, Singh et al. (1980) concluded that "the experimental technique involving a ^{7}Be/O_3 ratio to estimate the daily stratospheric component of ground-level O_3 is unverified and considered to be inadequate for air quality applications" (Singh et al., 1980, p. 1009). The investigators at SRI-International have suggested, however, that ^{7}Be may be used, under the appropriate meteorological conditions, as a qualitative tracer for air masses of stratospheric origin (Johnson and Viezee, 1981; Viezee et al., 1979).

Other methods have been used to estimate the quantitative contribution of stratospheric ozone to ozone concentrations measured at ground-level. These include: (1) aircraft observations of TF events (Johnson and Viezee, 1981), coupled with calculations of the downward flux of ozone in the troposphere (Viezee et al., 1983); (2) use of mean ^{90}Sr surface measurements, from radioactive fallout studies, to calculate a mean stratospheric ozone contribution (Reiter, 1978); and (3) examination of data, especially multiyear data, on surface ozone concentrations at remote sites (Viezee and Singh, 1982; Viezee et al., 1983). Using surface measurement data and their own data from aircraft measurements and calculated ozone fluxes, Viezee et al. (1983) concluded that direct ground-level impacts by stratospheric ozone may be infrequent, occurring <1 percent of the time; that such ground-level events are short-lived and episodic; and that they are most likely to be associated with ozone concentrations $\leq$0.1 ppm. Viezee et al. (1983) recommended further study, however, on the possible contribution at ground-level of stratospheric ozone.

On a qualitative basis, as mentioned earlier, there is no doubt that stratospheric ozone is present in the atmospheric surface layers, and the meteorological mechanisms that bring this about have been described by a number of investigators, including Wolff et al. (1979), Johnson and Viezee (1981), and others. Most investigators cite the basic meteorological analyses of Danielsen (1968) as a basis for their exchange model.

The downward transfer of air parcels and ozone from the stratosphere into the troposphere has been described above. There is, of course, a compensating transfer of tropospheric air upward into the lower stratosphere. Reiter (1975) has examined various mechanisms that contribute to this transfer. Air parcels moving out of the troposphere will carry with them the background concentrations of ozone that they had in the troposphere, and, as the air parcels mix in the stratosphere, these ozone molecules will become part of the stratospheric background ozone. Since the ozone concentrations are very much lower in the troposphere compared to the stratosphere, however, this exchange of tropospheric and stratospheric air parcels will not result in a net upward transport of ozone and is not considered to be a factor in air pollution situations.

3.4.8 Background Ozone from Photochemical Reactions

The apportionment of the background ozone concentrations measured at remote and other nonurban locations to stratospheric versus tropospheric processes and sources is the subject of continuing discussion and research. In addition, the apportionment of ozone produced photochemically in the troposphere to natural versus manmade sources of precursors, and, in turn, their respective contributions to background levels of ozone, also remain a focus of discussion and research. The preceding discussion has emphasized the thesis that the major source of tropospheric background ozone is the stratosphere. It must be recognized, however, that some investigators argue for a much larger role for the formation of significant amounts of ozone within the troposphere (e.g., Fishman et al., 1980; Fishman and Seiler, 1983; Fishman and Carney, 1984; Fishman et al., 1985; Fishman and Crutzen, 1978; Chameides and Walker, 1976). The question of the potential relative impacts of the stratospheric source of ozone and tropospheric photochemical sources has been evaluated critically by Singh et al. (1978, 1980).

Singh et al. (1980) concluded that background ozone in the troposphere is "principally of stratospheric origin," and supported this position with a number of arguments, including the following. First, the NO_x concentrations in the free troposphere appear to be very low, probably 0.01 to 0.1 ppb; at NO_x concentrations <0.03 ppb a tropospheric ozone reservoir cannot be generated, using photochemical simulation models. Second, Singh et al. (1980) pointed out that the tropospheric concentration pattern of ozone, with its spring maximum and fall minimum, is out of phase and inconsistent with a photochemical source, which would be at a maximum during the summertime peak of solar radiation flux. Also, at low latitudes, where the solar flux is relatively constant, the ozone seasonal cycle is quite pronounced and is consistent with the seasonal cycle of stratospheric-tropospheric exchange processes. In addition, Singh et al. (1980) noted that the vertical gradient of ozone in the troposphere is contrary to a dominant photochemical source for background tropospheric ozone.

Other evidence, however, especially more recent modeling studies, indicates that a substantial part of the O_3 measured during the warmer months of the year over the United States and Western Europe is of photochemical origin (Altshuller, 1986). Attempts to obtain agreement with observed O_3 concentrations with a general circulation model including only a stratospheric source of O_3 have been unsuccessful, especially over continents (Levy et al., 1985). From their tropospheric modeling studies, Fishman and coworkers have predicted the photochemical formation of near-surface, summer ozone at concentrations of:

(1) 40 ppb, using surface NO_x emissions corresponding to a concentration of ~0.25 ppb (Fishman and Seiler, 1983; Fishman and Carney, 1984); (2) 15 ppb, assuming zero NO_x emissions (Fishman and Seiler, 1983); and (3) 80 ppb, using NO_x emissions corresponding to a concentration of about 5 ppb and ignoring contributions from individual urban or industrial plumes (Fishman et al., 1985). Using another model, Dignon and Hameed (1985) have predicted the photochemical production of ozone at midlatitudes of the Northern Hemisphere at annual average concentrations of: (1) $\lesssim$60 ppb, using a 1980 NO_x emissions inventory; or (2) ~25 ppb, assuming zero manmade NO_x emissions. On the basis of his review of these and other studies, Altshuller (1986) has estimated that average stratospheric contributions to near-surface ozone concentrations range from 10 to 15 ppb.

As these data and the preceding discussion in Section 3.4.7 indicate, the portion of background ozone concentrations attributable to stratospheric sources versus tropospheric photochemistry remains uncertain, especially in the absence of a quantitative technique for determining whether ozone is of stratospheric origin.

Investigations on the contributions of photochemistry to background ozone have focused on (1) the role of transport from urban into nonurban areas, which was discussed in Section 3.4 (see also Chapter 5); and (2) the respective roles of biogenic VOC and of NO_x, from all sources, in the photochemical formation of ozone in nonurban areas.

Altshuller (1983) has evaluated the specific question of whether naturally emitted VOC (i.e., from biogenic VOC sources) could be a significant source of background ozone. Since biogenic emissions are released into the atmospheric boundary layer, this potential source of ozone is expected to affect only ground-level or boundary-layer concentration patterns, in contrast to the whole troposphere as described in the preceding discussion. While a matter of controversy in recent years, the data on the role of biogenic VOC in boundary-layer photochemistry now appear more conclusive. Inventories of biogenic VOC emissions indicate that they are of the same order of magnitude as manmade VOC emissions, as described in Section 3.5.1 (below). On the other hand, concentration data indicate that biogenic VOC occur, even in nonurban areas, at low levels in ambient air relative to VOC from manmade sources (Section 3.5.2 below). In an extensive review of the literature, Altshuller (1983) noted that the concentrations of biogenic hydrocarbons are very low, constituting even at rural sites probably 10 percent or less of the total nonmethane hydrocarbons. He concluded that the contribution of biogenic hydrocarbons to ozone formation, as a result, does not appear to be significant under most atmospheric conditions.

The role of NO_x in the photochemical formation of ozone in nonurban areas has been the subject of a number of modeling and experimental studies, as well as a recent review (Altshuller, 1986). As summarized in Section 3.5 (below), and as reviewed by Altshuller (1986), NO_x concentrations in nonurban areas of the United States are appreciably lower than those in urban areas, sometimes by an order of magnitude. Likewise, concentrations of NO_x in the western United States are usually lower by about a factor of ten than those in the northeastern states (Section 3.5.2.2.2). At nonurban locations inside of populated areas, however, the concentrations of NO_x are much higher than those measured in clean air within the continental and maritime boundary layer and in the free troposphere (Altshuller, 1986).

Global background concentrations of NO_x were previously thought to be lower than more recent measurements show them to be. For example, the analysis cited earlier in this section (Singh et al., 1980), on the contributions of photochemistry versus stratospheric intrusions, assumed NO_x concentrations in the free troposphere of 0.01 to 0.1 ppb and an NO_x reservoir of <0.03 ppb; and the global models described in Kelly et al. (1984) assume an NO_x background of 0.1 to 0.2 ppb. In contrast, the mean NO_x concentrations tabulated by Altshuller (1986) for remote surface sites, while ≤ 1 ppb and often <0.5 ppb, are still in excess of the ranges described above. At nonurban sites east of the Rocky Mountains in the United States, mean NO_x concentrations range from 1 to 10 ppb (Altshuller, 1986).

Martinez and Singh (1979) analyzed the role of NO_x in nonurban ozone formation using theoretical approaches and aerometric data from the Sulfate Regional Experiment. They concluded that the impact of NO_x on nonurban ozone is a function of geographical location since ozone production was NO_x-limited at some sites they examined but not at others. Kelly et al. (1984) examined the role of photochemistry in nonurban ozone at three very different rural sites (in South Dakota, Louisiana, and Virginia, respectively) by ambient air analyses, captive air irradiations, and photochemical modeling. Ambient air analyses indicated the formation of about 6 ppb ozone per ppb of NO_x. Irradiation and modeling results indicated similar, but slightly higher, ozone formation per ppb of initial NO_x. They concluded that photochemistry in these rural areas was not NO_x-limited but depended, as well, on hydrocarbon concentrations. In a study that included modeling and a comparison of the modeled predictions with observed ozone concentrations, Liu et al. (1984) arrived at a similar conclusion; i.e., that nonurban ozone formation in the areas they studied was not exclusively controlled by the equilibrium between NO_x and ozone (Equation 3-4, Section 3.3.1) but by the hydrocarbon reactions, as well. Consistent with the results of the Kelly et al. (1984) study, Parrish et al. (1986) developed empirical relationships between ozone and NO_x concentrations (June to September) at a high-altitude location (Niwot Ridge, Colorado) and found the photochemical formation of about 17 ppb ozone for each ppb of NO_x.

The studies and analyses cited in this and the preceding section indicate that research is still needed to permit the apportionment of background ozone to stratospheric and respective tropospheric sources. From his review of data pertinent to the role of NO_x in boundary-layer photochemistry, Altshuller (1986) concluded that photochemically generated ozone should equal or exceed ozone transported down from the stratosphere to relatively remote locations at lower elevations. At more polluted rural locations, photochemically generated ozone from manmade emissions are predicted to constitute most of the ozone measured during the warmer months of the year. Thus, the evidence supporting the stratosphere as being the major (but not exclusive) source for background tropospheric ozone is relatively strong but still not conclusive. Research in these topic areas is continuing, and the number of uncertainties and necessary assumptions needed for the respective conclusions cited above should be reduced as new data become available.

3.5 PRECURSORS TO OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

3.5.1 Sources and Emissions

3.5.1.1 Manmade Sources and Emissions. This section presents information on the manmade sources and emissions of precursors to ozone and other photochemical oxidants. Estimates of annual emissions are presented by source category for volatile organic compounds and nitrogen oxides. In addition, information is presented on emission rates and the composition of emissions from principal stationary sources and from mobile sources. The annual estimates are based on emission inventories prepared according to procedures developed and published by EPA (U.S. Environmental Protection Agency, 1980a,b; 1981a,b,c,d,e,f).

3.5.1.1.1 Trends in emissions of volatile organic compounds. Emission data on volatile organic compounds (VOC) include data on hydrocarbons as well as other organic compounds found in ambient air. Because of their negligible reactivity toward the photochemical production of ozone, methane, ethane, methylene chloride, and several halogenated methanes and ethanes are also excluded from emission inventories (U.S. Environmental Protection Agency, 1980b). Estimates of total emissions of volatile organic compounds (VOCs) provide a gross measure of compounds available for photochemical production of ozone and other photochemical oxidants. Emissions of VOCs are reported here as the collective mass of reactive VOC. (See the footnote to Table 3-8 for the calculation of emissions-based $NMOC/NO_x$ ratios.)

Retrospective estimates of total manmade VOC emissions in the United States, based on records of economic activity (e.g., fuel usage, industrial production) have been prepared by decade, beginning with 1940 (U.S. Environmental Protection Agency, 1986). From a level of 18.5 Tg/yr in 1940, VOC emissions increased about 14 percent each decade through 1970, then began to decline (Table 3-8).

Figure 3-14 shows national trends in yearly emissions of manmade VOC by general source category for the period 1970 through 1983 (U.S. Environmental Protection Agency, 1984a). Emissions in 1983 of manmade VOCs in the United States have been estimated at 19.9 Tg/yr (U. S. Environmental Protection Agency, 1984a); total manmade VOC emissions nationwide were 26 percent lower in 1983 than in 1970. The observed decrease is attributable largely to a decrease of 30 percent in estimated VOC emissions from highway vehicles during this period. This decrease occurred in spite of a 42 percent increase in vehicle miles traveled. Trends in manmade VOC emissions versus vehicle miles traveled, urban only and total, for 1970 through 1983, are shown in Figure 3-15 (U.S. Environmental Protection Agency, 1984a; Motor Vehicle Manufacturers Association, 1984). The main sources nationwide of manmade VOC are industrial processes, which emit a wide variety of VOCs such as chemical solvents; and transportation, which includes the emission of VOCs in gasoline vapor as well as in gasoline combustion products.

3.5.1.1.2 Trends in emissions of nitrogen oxides. Emissions of nitrogen oxides (NO_x) are reported here as the sum of NO and NO_2, all expressed as equivalent NO_2. Retrospective estimates of total manmade NO_x emissions in the

TABLE 3-8. EMISSIONS OF VOC BY DECADE, 1940 THROUGH 1980 (Tg/yr)[a]

Source category	1940	1950	1960	1970	1980
Transportation	5.2	7.9	11.1	12.3	8.2
Stationary fuel combustion	4.7	3.1	1.9	1.0	2.1
Industrial processes	3.2	5.2	6.1	8.7	8.9
Solid waste	0.9	1.0	1.4	1.8	0.6
Miscellaneous	4.5	3.6	3.1	3.3	2.9
Total	18.5	20.8	23.6	27.1	22.7

Source: U.S. Environmental Protection Agency (1986).

[a] To calculate emissions-based NMOC/NO_x molar ratios, as used in control-related data, a multistep procedure is required (Novak, 1986) as described by the equation:

$$\text{Total NMOC (Tg/yr)} \times \mathrm{SUM}_{i=1}^{4}[\mathrm{Pct}_i \times \mathrm{no.}_i/\mathrm{mw}_i]/[\text{Total } NO_x \text{ (Tg/yr)}/46]$$

where Pct = percent of a compound class present in the NMOC emissions;
no. = average carbon number for a compound class;
mw = average molecular weight for a compound class;
i represents the four compound classes of interest; and
NO_x emissions are expressed as NO_2 (mw = 46).

Values for terms in the equation vary in the published literature. Example values, where no. and mw are derived from emissions inventories (Novak, 1986) and pct from ambient air concentration data (Richter, 1986), are: paraffins = [63.5 x 4.56/95]; olefins = [15.5 x 3.57/43]; aromatics = [15.5 x 7.56/97]; and aldehydes = [2.0 x 1.5/37].

United States have been prepared by decade, beginning with 1940 (U.S. Environmental Protection Agency, 1986). From a level of 6.8 Tg/yr in 1940, NO_x emissions increased almost 40 percent each decade through 1970 (Table 3-9). The increase from 1970 to 1980 was 13 percent.

Total NO_x emissions in the United States in 1983 (19.4 Tg/yr) were some 17 percent above the 1970 level, but appear to have declined slightly from about 1980 through 1983 (Figure 3-16) (U.S. Environmental Protection Agency, 1984a). The net increase over the period 1970 through 1983 may be attributed primarily to two causes: (1) increased fuel combustion in stationary sources such as power plants; and (2) increased fuel combustion in highway motor vehicles, as the result of the increase (42 percent) in vehicle miles driven over the 14 years in question. Emissions associated with industrial processes

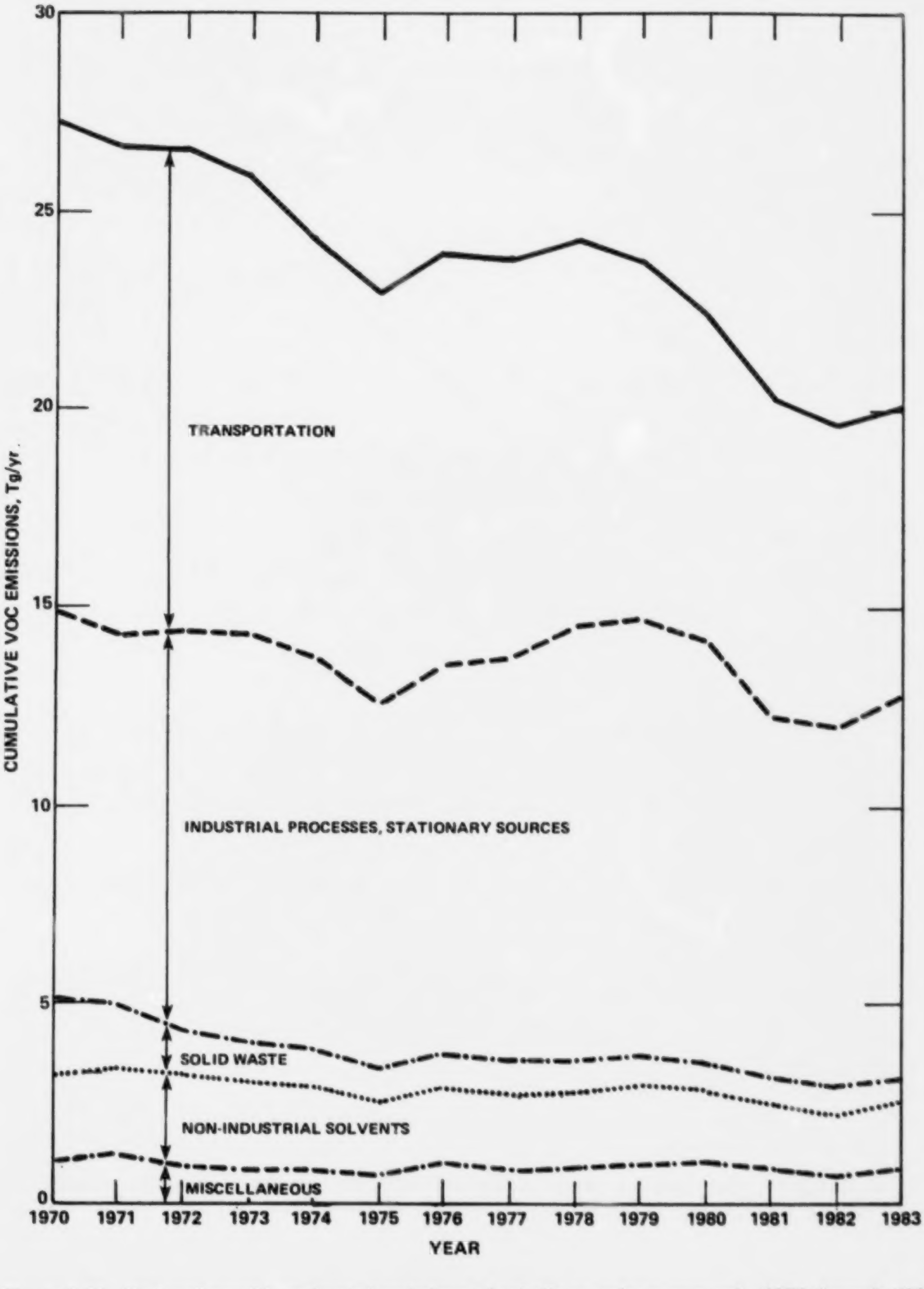


Figure 3-14. National trend in estimated emissions of volatile organic compounds, 1970 through 1983.

Source: U.S. Environmental Protection Agency (1984a).

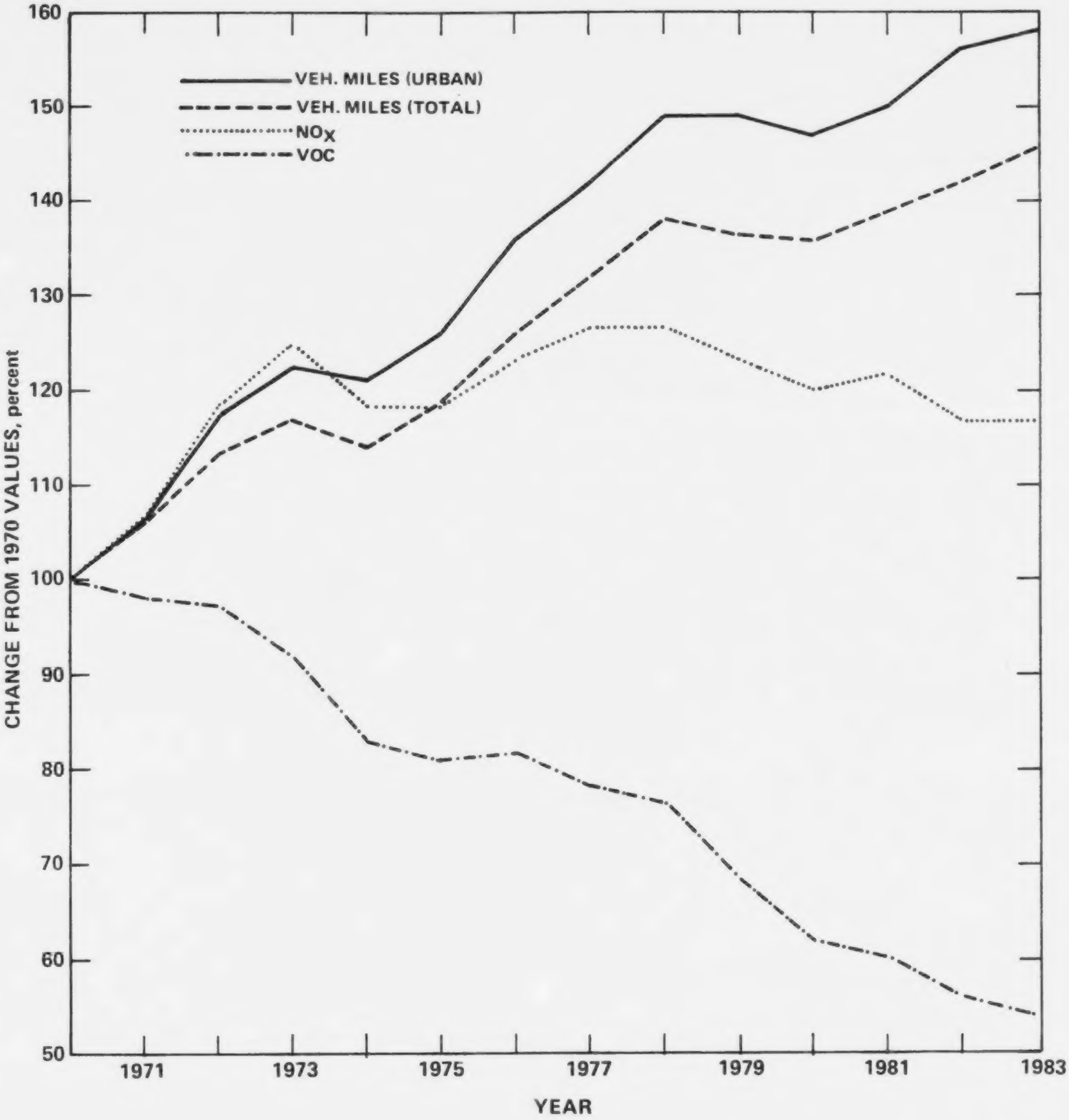


Figure 3-15. Comparative trends in highway vehicle emissions of nitrogen oxides (NO_X) and volatile organic compounds (VOC) versus vehicle miles traveled, 1970-1983.

Source: Motor Vehicle Manufacturers Association (1984); U.S. Environmental Protection Agency (1984a).

TABLE 3-9. EMISSIONS OF NO_x BY DECADE, 1940 THROUGH 1980
(Tg/yr)

Source category	1940	1950	1960	1970	1980
Transportation	2.2	3.5	4.9	7.6	9.2
Stationary fuel combustion	3.4	4.7	6.7	9.1	10.2
Industrial processes	0.2	0.3	0.5	0.7	0.7
Solid waste	0.1	0.2	0.3	0.4	0.1
Miscellaneous	0.9	0.6	0.4	0.3	0.2
Total	6.8	9.3	12.8	18.1	20.4

Source: U.S. Environmental Protection Agency (1986).

remained relatively constant, but solid waste and miscellaneous emissions decreased slightly.

The national trends shown do not reflect the considerable local and regional differences that exist in the relative amounts of NO_x emitted in the major source categories. For example, motor vehicle emissions in Los Angeles County, California, increased sixfold from 1940 to 1970 (Los Angeles County, 1971), compared to a threefold national increase. Figure 3-15 compares the relative trends in mobile source NO_x emissions versus vehicle miles traveled, urban only and total, from 1970 through 1983 (U.S. Environmental Protection Agency, 1984a; Motor Vehicle Manufacturers Association, 1984).

3.5.1.1.3 Sources and emissions of volatile organic compounds. The source category contributing the largest percentage of VOC emissions in 1983, 37.7 percent, is Industrial Processes (U.S. Environmental Protection Agency, 1984a). The category consists almost entirely of point sources. The composition of these emissions varies widely, depending on the process or product and the use of emission reduction equipment and operating practices.

The second largest VOC source category, Transportation, accounting for 36.2 percent of the annual total in 1983, is discussed below.

The third largest VOC source category, Miscellaneous, accounts for 12.6 percent of the annual total, over half of which consists of the subcategory, Miscellaneous Organic Solvents (U.S. Environmental Protection Agency, 1984a). These emissions generally qualify as area-source emissions. Some of these solvents are widely used in domestic products such as furniture polish, shoe polish, shaving soap, perfumes, cosmetics, shampoo, hair spray, hand lotion,

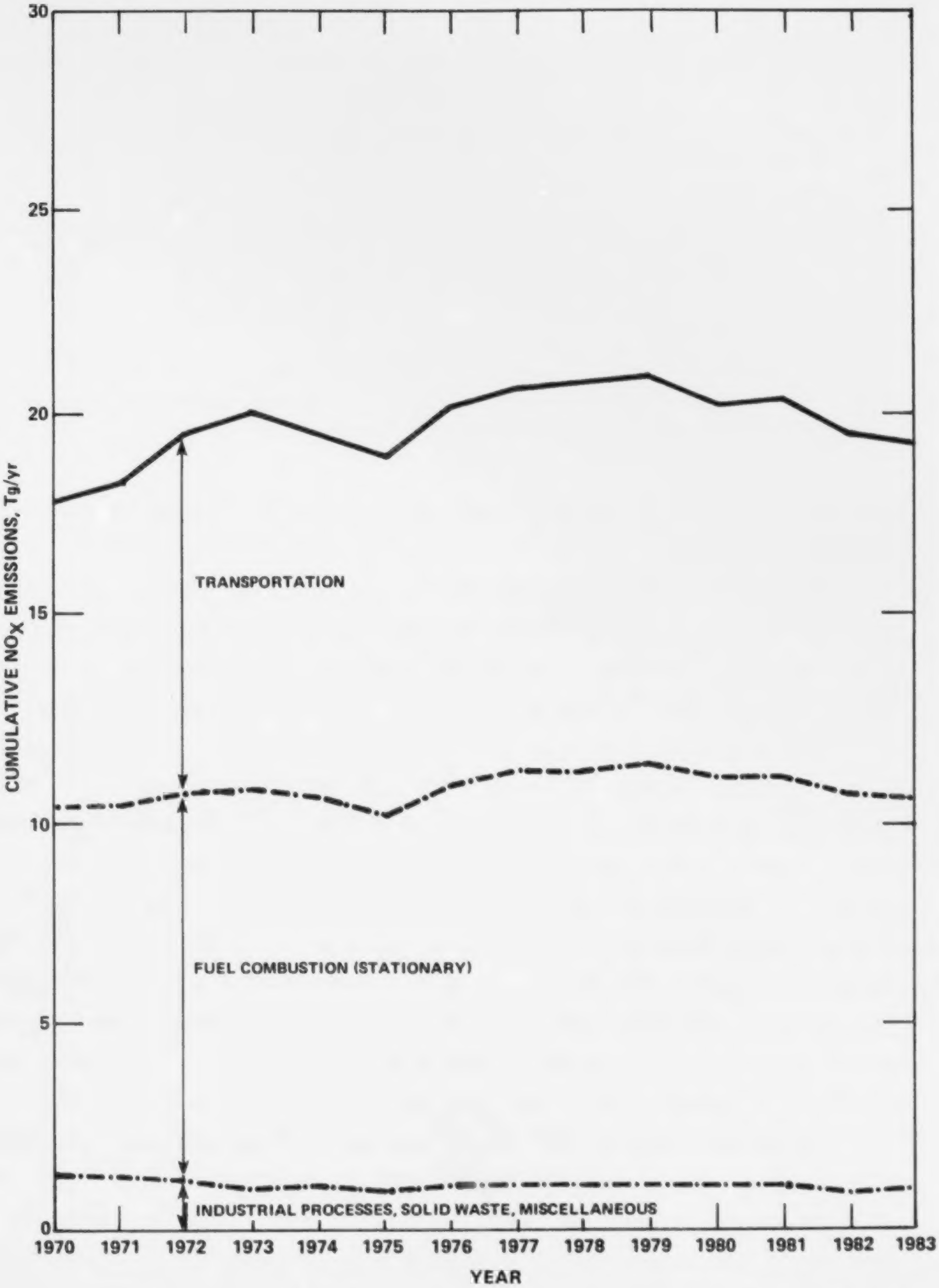


Figure 3-16. National trend in estimated emissions of nitrogen oxides, 1970 through 1983.

Source: U.S. Environmental Protection Agency (1984a).

rubbing alcohol, and nail polish remover. The predominant compounds emitted are isopropyl alcohol and ethyl alcohol (Bucon et al., 1978).

Emissions of volatile organic compounds from the production and marketing of gasolines and motor oils are classed in the Industrial Processes category of VOC emissions. Emissions of VOC from these petroleum products after their sale to vehicle owners are included in the Transportation category.

A significant portion of VOC emissions from gasoline-fueled mobile sources arises from evaporation, but the most conspicuous mobile source emissions are the combustion products. In a study by Black et al. (1980), evaporative emissions were found to constitute one-third to one-half of total hydrocarbon emissions from all of the vehicles tested (n = 60). Based upon actual surveillance tests of in-use vehicles, Fisher (1980) found emission rates of 2.53 g/mi in 1968 and 0.15 g/mi in 1980 for composite evaporative and crankcase emissions from gasoline-fueled cars.

Exhaust emissions from gasoline-fueled vehicles typically contain fuel components and low-molecular-weight hydrocarbons that are not present in the fuel. Typically, exhaust from a catalyst-equipped automobile contains about 62 percent alkanes, 17 percent aromatics, 18 percent alkenes, and 3 percent acetylene. This may be compared with the corresponding typical values for automobiles without converters: 40, 24, 26, and 11 percent, respectively. Methane levels generally range from about 10 to 30 percent (Black and Bradow, 1975; Black, 1977). Exhaust gases from gasoline-fueled vehicles also contain organic compounds such as aldehydes, ketones, ethers, esters, acids, and phenols, amounting to as much as one-tenth of the total VOC content.

Factors other than gasoline composition influence the composition of exhaust from internal combustion engines. These include driving patterns, the specific configuration of emission control devices, ambient temperature and humidity, and, of course, individual automobile parameters such as tuning, make, and model year. Fuel additives can also influence emissions. For example, in one study, tetraethyl lead increased hydrocarbon emissions by about 5 percent but did not change the type of emissions (Leihkanen and Beckman, 1971).

Evaporative emissions from diesel vehicles are negligible because of low fuel volatility (Linnell and Scott, 1962; McKee et al., 1962). In studies of exhaust emissions from diesel automobiles (Black and High, 1979; Gibbs et al., 1983), 15 to 40 percent of the hydrocarbons emitted were found to be associated with particles by the time the exhaust stream exited the tailpipe. Gibbs et al. (1983) reported THC emissions from 19 in-use diesel automobiles, representing 1977 to 1979 model years, that were tested periodically over a 28-month period. Emissions of THC at the end of the period ranged from 0.17 to 0.88 g/mi for individual vehicles and averaged 0.65 g/mi. It should be noted here that the population of diesel-powered passenger cars is not growing as rapidly as expected. Sales of diesel-powered cars peaked at 6 percent for 1981 models and dropped to less than 3 percent by 1983 (Automotive News, 1982a,b,; 1983a,b; Plegue, 1983).

A brief summary of both exhaust and evaporative emissions characteristic of a variety of engines, fuel types, and control devices has been presented by Tilton and Bruce (1981). Their summary indicates, for example, that exhaust emissions of aldehydes and ethylene increase in cars fueled with ethanol-gasoline blends (gasohol) as opposed to gasoline. Exhaust emissions of total hydrocarbons (THC) decrease but evaporative emissions increase, for a net increase in emissions from gasohol-fueled cars. In diesels, evaporative THC emissions are virtually nonexistent, and net exhaust emissions of THC are lower. The percentage of carbonyl compounds (aldehydes, ketones) in the exhaust of diesels is higher than from gasoline combustion, but the net photochemical reactivity per gram of emissions is lower nevertheless (Tilton and Bruce, 1981).

In view of changes in emissions with fuel type, it is of interest to examine fuel usage in the United States in recent years. Yearly sales of vehicle fuels fluctuate in consequence of several factors, including retail fuel price, general economic conditions, and the age and fuel efficiency of the composite vehicle population. In addition to the year-to-year influence of these factors on the sales of the principal vehicle fuels, gasoline and diesel fuel, a change in fuel composition is emerging with the introduction in the United States of gasolines containing a percentage of ethanol. As shown in Table 3-10, sales of gasoline containing up to 10 percent ethanol (gasohol) were first reported in 1981 and had increased almost sixfold 2 years later (NPN: National Petroleum News, 1981-1985 summary issues).

3.5.1.1.4 Sources and emissions of nitrogen oxides. Fuel combustion is the dominant source of NO_x emissions nationally. Stationary sources contributed 50 percent and mobile sources contributed 45.4 percent in 1983 (U.S. Environmental Protection Agency, 1984a). In contrast to their contributions to VOC

TABLE 3-10. YEARLY QUANTITIES OF MOTOR VEHICLE FUELS SOLD IN THE UNITED STATES FOR HIGHWAY USE, 1980 THROUGH 1983

Fuel	Gallons x 10^9			
	1980	1981	1982	1983
Gasoline	106.45	104.14	100.70	101.55
Gasohol	--	0.72	2.16	4.29
Diesel	13.60	14.30	14.67	15.87

Source: NPN: National Petroleum News (1981-1985 summary issues).

emissions, industrial process sources contributed only about 3 percent to the national total of manmade NO_x emissions in 1983 (U.S. Environmental Protection Agency, 1984a).

Ratios of NO/NO_x in emissions vary depending upon the source. Nitric oxide (NO) is the dominant oxide of nitrogen emitted by most sources; NO_2 generally comprises less than 10 percent of the total NO_x emissions. More than 30 to 50 percent, however, of the total NO_x emissions from certain diesel (Braddock and Bradow, 1976; Springer and Stahman, 1977 a,b) and jet turbine engines (Souza and Daley, 1978) can be NO_2 under specific load conditions. Likewise, tail gas from nitric acid plants, if uncontrolled, may contain about 50 percent NO_2 (Gerstle and Peterson, 1966). Variations in NO/NO_x ratios by source type can be significant in local situations, as, for example, in the immediate vicinity of a high-volume roadway carrying a significant number of diesel-powered vehicles.

Emissions of NO_x from the principal categories of stationary combustion sources, electric utility boilers, industrial boilers, and industrial process heaters, vary according to fuel type and equipment design. Among electric utility boilers, coal-fired units produce the highest NOx emissions (994 ppm), as reported by Bartok et al. (1971). Combustion modifications can reduce NOx emissions from such coal-fired units by 50 percent (Crawford et al., 1974, 1978). Coal-fired industrial boilers also emit greater amounts of NOx (475 ppm) than oil-fired units emit (Cato et al., 1974, 1976). Of the industrial process heaters studied by Hunter et al. (1978, 1979), cement kilms emitted the highest levels of NOx (90 to 2250 ppm).

Seasonal variations in NO_x emissions from stationary sources are expected since power plants using fossil fuels produce an estimated 15 percent more NO_x

in the summer than in the spring (U.S. Department of Energy, 1978). Greater degrees of variation and different seasonal patterns have been reported for stationary sources in different regions of the country (California Board of Sanitation, 1966).

Emissions of NO_x from mobile sources, gasoline- and diesel-fueled vehicles, are affected by a number of variables such as speed, load, and air:fuel ratio (AFR), as reported by Hilliard and Wheeler (1979). Seasonal variations in NO_x emissions from mobile sources will occur in relation to temperature (about a 35 percent decrease in emissions per vehicle mile with an ambient temperature increase from 20 to 90°F) (Ashby et al., 1974), and number of vehicle miles traveled (about 18 percent higher in summer than in winter, nationwide) (Federal Highway Administration, 1978). Emissions of NO_x also vary with vehicle miles traveled in urban versus rural areas and among states in different regions of the country (Federal Highway Administration, 1978). Diurnal variations in NO_x emissions associated with motor vehicle traffic are especially important because of their potential impact on ambient air quality. Table 3-11 summarizes data on NO_x emissions from mobile sources.

TABLE 3-11. SUMMARY OF NO_x EMISSIONS FROM MOBILE SOURCES

Vehicle type	Emissions, g/mi	Comments	Reference
Gasoline-fueled passenger cars	0.41 to 1.84	In-use; equipped with three-way catalysts; four test cycles used	Smith and Black, 1980
Diesel passenger cars	0.84 to 3.15	In-use, 1977 to 1979 model years; tested at ca. 35,000 mi	Gibbs et al., 1983
Heavy-duty trucks			
Gasoline (leaded)	12.29 to 15.58	One test cycle	Dietzman et al., 1980, 1981
Diesel	17.47 to 42.40	One test cycle; several diesel fuels	

3.5.1.2 Natural Sources and Emissions

3.5.1.2.1 Natural sources and emissions of volatile organic compounds. This section presents a brief overview of the nature and quantity of hydrocarbon emissions from biogenic sources. For detailed information, the reader is referred to several excellent review articles (Altshuller, 1983; Bufalini and Arnts, 1981; Dimitriades, 1981).

To date, isoprene and the monoterpenes are the only biogenic hydrocarbons identified as emissions from vegetation (e.g., Sanadze and Dolidze, 1962; Rasmussen, 1964, 1970; Evans et al., 1982). Other volatile organic emissions from vegetation have been documented, but consist of oxygenated organic compounds, e.g., camphor and 1,8-cineole (see, e.g., Graedel, 1978). Isoprene and the monoterpenes are of interest to atmospheric scientists largely because they are volatile enough to be released under normal environmental conditions, because they are abundant relative to other biogenic VOCs, and because they have been shown to be potential ozone precursors. The commonly identified monoterpenes are α-pinene, β-pinene, camphene, Δ^3-carene, limonene, myrcene, and β-phellandrene. As a general rule, coniferous trees emit primarily monoterpenes, and deciduous trees emit isoprene.

Biogenic emission rates. Biogenic emission rates have been determined almost exclusively by techniques that involve enclosing the entire plant or a portion of it, such as a branch of a tree, in a bag or chamber constructed of light, transparent material. Isoprene and monoterpene emission rates given here [as μg (g dry biomass)$^{-1}$ hr^{-1}] were measured by the enclosure method. Because biogenic emission rates are species- and temperature-dependent, the species tested and the enclosure temperature are also given.

Isoprene emission rates reported by Evans et al. (1982) for various species of trees range from 3 $\mu g\ g^{-1}\ hr^{-1}$ for spruce (Picea sitchensis, 28°C) to 233 $\mu g\ g^{-1}\ hr^{-1}$ for willow (Salix babylonica, 30°C). Reported emission rates for oak range from 9 $\mu g\ g^{-1} hr^{-1}$ (Quercus virginiana, 30°C; Zimmerman, 1979) to 49 $\mu g\ g^{-1}\ hr^{-1}$ (Quercus agrifolia, 30°C; Winer, 1983). The reader is referred to the studies by Zimmerman (1979), Evans et al. (1982), and Winer (1983) for additional rate data and experimental details.

Monoterpene emission rates are probably best-documented for pine. Rates obtained by Winer (1983) ranged from 0.6 $\mu g\ g^{-1}\ hr^{-1}$ (Pinus radiata and Pinus halepensis, 30°C) to 2 $\mu g\ g^{-1}\ hr^{-1}$ (Pinus canariensus, 30°C). For Pinus taeda, Arnts et al. (1978) reported a rate of 4 $\mu g\ g^{-1}\ hr^{-1}$ (at 30°C) and Knoppel et al. (1982) reported a rate of 1 $\mu g\ g^{-1}\ hr^{-1}$ (at 30°C). Among the higher monoterpene emission rates are those for Pinus clausa, 11 $\mu g\ g^{-1}\ hr^{-1}$ at 30°C (Zimmerman, 1979) and for Douglas fir (Pseudotsuga taxifolia), 15 $\mu g\ g^{-1}\ hr^{-1}$ at 30°C (Knoppel et al., 1982). See also the studies by Rasmussen (1972) and by Evans et al. (1982) for additional monoterpene emission rate data.

Besides temperature, biogenic emission rates are affected by other environmental factors. Rasmussen (1972) reported that emission rates varied with species, plant maturity, resin gland integrity, and leaf temperature. Dement et al. (1975) found that the emission rate of monoterpenes from Salvia mellifera (California Black Sage) is dependent on the vapor pressures of the terpenes, the humidity, and the amount of oil present on the surface of the leaf; but found that the emission rate is not directly dependent on the photosynthetic activity or on the stomatal openings of the plant.

Tingey and his coworkers, in extensive studies on factors effecting isoprene emission rates in live-oak seedlings (Tingey et al., 1981), found light intensity to be a chief determinant of emissions, which decreased to near zero levels in the dark. In contrast to isoprene, monoterpene emission rates did not appear to be influenced by light intensity but were affected by temperature (Tingey et al., 1980); a log-linear increase in emission rates of monoterpenes with temperature was observed in studies of slash pine.

The validity of emission rate data obtained by the bag enclosure technique has been widely discussed because of uncertainties associated with (1) isolating the vegetation in an artificial environment; (2) possible damage to isolated vegetation; (3) representativeness of emission rates measured from just one branch; and (4) relationship of emission rates to ambient air concentrations of biogenic hydrocarbons.

Attempts to validate the bag enclosure method have focused on comparing enclosure emission estimates with those obtained by alternate procedures, such as micrometeorological gradient procedures (e.g., Lamb et al., 1983; Knoerr and Mowry, 1981). In a study of Pennsylvania hardwood forest, the gradient profile procedure gave a flux of 8,000 $\mu g\ m^{-2}\ hr^{-1}$, while the enclosure technique yielded 7,300 $\mu g\ m^{-2}\ hr^{-1}$ (Lamb et al., 1983). Good agreement has been reported, also, for α-pinene emission fluxes measured by a micrometeorological procedure and by the enclosure method (Knoerr and Mowry, 1981).

Although the micrometeorological approach yields mass fluxes similar to the enclosure method, it, too, has certain limitations. For example, the measurement of small vertical gradients above a forest canopy and the application of surface layer theory to non-ideal sites can lead to erroneous results. Such difficulties can largely be avoided by simulating the forest emissions with an inert tracer release (such as SF_6) and measuring ambient concentrations of the tracer and biogenic gases along downwind sample lines (e.g., Arnts and

Meeks, 1981). Isoprene fluxes obtained using the tracer procedure in a central Washington oak grove compared well with flux estimates determined simultaneously with the enclosure technique (Allwine et al., 1983).

Biogenic emission inventories. Development of a biogenic emission inventory requires knowledge of (1) emission rates for individual species; (2) the vegetation coverage of an area, by species; (3) leaf biomass per tree (derived through allometric equations); and (4) a biomass factor for the forested area (derived from (2) and (3).

Table 3-12 contains a listing of area-wide biogenic emission fluxes that have been reported for the United States and portions thereof. Accuracy of the estimates reported in Table 3-12 depends upon the size of the area for which the inventory has been prepared. Many of the problems and uncertainties encountered in preparing inventories have been discussed in detail in the literature (Altshuller, 1983; Zimmerman, 1979, 1980; Wells, 1981; Box, 1981; Dimitriades, 1981).

TABLE 3-12. AREA-WIDE BIOGENIC EMISSION FLUXES

Location	Emission flux, μg $m^{-2}hr^{-1}$	Comment	Reference
South Coast Air Basin, California	≤ 780		Winer (1983)
Lake Tahoe, California	1950	Entire basin	JSA, Inc. (1978)
Lake Tahoe, California	2438	Forested area of basin	JSA, Inc. (1978)
San Francisco Bay Area, California	1388		Sandberg et al. (1978)
San Francisco Bay Area, California	2265	Daytime	Hunsaker (1981)
San Francisco Bay Area, California	777	Nighttime	Hunsaker (1981)
Tampa/St. Petersburg, Florida	2540		Zimmerman (1979)
Southeastern Virginia	8890	Forested area only	Salop et al. (1983)
Pennsylvania	1660		Flyckt et al. (1980)
Houston, Texas	1170		Zimmerman (1980)
United States	1712		Marchesani et al. (1970)
United States	1099		Zimmerman (1977)
United States	884		Zimmerman (1978)

Considering all the variables that affect biogenic emissions and their inventories, it is somewhat surprising that the area-wide emission fluxes listed in Table 3-13 show no more variation than they do. With the exception of the Southeastern Virginia area, which is a forested region with high biomass coverage, most of the values in Table 3-12 differ by less than a factor of three.

3.5.1.2.2 Natural sources and emissions of nitrogen oxides. Natural emissions of nitrogen oxides (NO_x) originate from the oxidation of nitrogen gas by electrical discharge in the atmosphere, from the ammonification of organic nitrogen during biological decomposition, and from the oxidation of organic nitrogen during forest fires. Nitrogen fixation and electrical discharge are normal processes of the nitrogen cycle that convert inert nitrogen gas to biologically useful nitrate or ammonia. For a discussion of the nitrogen cycle relative to NO_x emissions, the reader is referred to Air Quality Criteria for Nitrogen Oxides (U. S. Environmental Protection Agency, 1982a). Table 3-13 provides estimates of some of the nitrogenous compounds emitted from respective transformation processes.

Although 40 to 108 tg NO_x-N per year has been estimated to be released from terrestrial sources to the atmosphere, the bulk is reabsorbed and only 8 to 25 Tg NO_x-N escapes to the troposphere (Robinson and Robbins, 1975; Söderlund and Svensson, 1976). Hill (1971) reported that NO and NO_2 are absorbed, to some extent, from the atmosphere by plants. Using data obtained from the experiments of Marakov (1969), and those of Kim (1973), Söderlund and Svensson (1976) estimated that soil contributes to the atmosphere between 1 and 14 Tg N in the form of NO and NO_2. They also hypothesized that a net flow occurs of NO_x from terrestrial to aquatic systems, but concluded that losses from aquatic ecosystems to the atmosphere are insignificant. The principal source of gaseous NO_x in terrestrial systems is believed to be the decomposition of nitrates (Söderlund and Svensson, 1976).

Although more is known about the natural biological and chemical processes in the environment that produce emissions of nitrogen oxides than those that produce VOC, the problems with actually quantifying such emissions exceed the problems associated with quantifying natural emissions of VOC. As indicated in Chapter 4, the limits of detection of methods for measuring nitrogen oxides are such that low-level measurements are often not reliable. Techniques for estimating NO_x emissions from such sources as lightning and biological processes

TABLE 3-13. GLOBAL ESTIMATES OF NITROGEN TRANSFORMATION
(Tg N/yr)

	Range of estimates	References[a]
Biological fixation ($N_2 \rightarrow NH_4^+$)	54 to 270	1-5
Electrochemical fixation		
lightning ($N_2 \rightarrow NO_x$)	10 to 40	2, 6, 7, 8, 10
atmospheric ($N_2 \rightarrow NO_2$)	14 to 20	2, 4
Biological denitrification		
($NO_3^- \rightarrow N_2$)	96 to 190	2, 3
($NO_3 \rightarrow N_2O$)	20 to 340	2-4
combined	83 to 270	5, 8, 9
Industrial denitrification		
(Organic -N $\rightarrow NO_x$)	14 to 19	2-4
(Other $\rightarrow NO_x$)	30 to 36	2, 3, 5
Atmospheric denitrification ($NH_3 \rightarrow NO_x$)	3 to 30	2, 3
Natural NO_x emissions from land and sea	40 to 210	3, 4
NH_3 emissions to atmosphere from land and sea	110 to 850	2-4

[a] 1. Delwiche (1970).

2. Burns and Hardy (1975).

3. Söderlund and Svensson (1976).

4. Robinson and Robbins (1975).

5. Liu et al. (1977).

6. Crutzen and Ehhalt (1977).

7. Noxon (1976).

8. Sze and Rice (1976).

9. Council for Agricultural Science and Technology (1976).

10. Chameides et al. (1977).

are virtually nonexistent. In addition, scaling of emissions from such sources as bacterial nitrification and denitrification for use in preparing area-wide emission inventories is not possible. Thus, the emissions reported in this section should be taken as very gross approximations that serve to identify natural sources of NO_x and to present the estimated relative magnitude of emissions from such sources.

3.5.2 Representative Concentrations of Ozone Precursors in Ambient Air

As discussed earlier in this chapter (Section 3.3), nonmethane organic compounds (NMOC) and the oxides of nitrogen (NO_x) in the presence of sunlight react to form ozone and other photochemical oxidants. The reaction sequence is complex, so that dependable precursor-oxidant relationships are difficult to establish. Factors such as absolute NMOC and NO_x concentrations, relative NMOC and NO_x concentrations (NMOC/NO_x ratios), NMOC reactivity, and NO_x composition are known to affect the photochemical reactions that produce ozone and other oxidants in ambient atmospheres. Concentration-based NMOC/NO_x ratios are used in some precursor-oxidant models. Ratios of NMOC/NO_x that are concentration-based are calculated directly, using measured concentrations of NO_x expressed as NO_2 (ppm or ppb) and measured concentrations of hydrocarbons expressed as carbon (ppm or ppb C). The latter is easily obtained from gas-chromatographic measurements, since the chromatograph yields a known response per carbon atom. This section provides summaries of NMOC and NO_x concentrations recorded at various urban and nonurban locations in the United States. In addition, HC/NO_x (or NMOC/NO_x) ratios are given for some urban areas.

3.5.2.1 Concentrations of Nonmethane Organic Compounds in Ambient Air. The NMOC data in this section are segregated into (1) nonmethane hydrocarbons (NMHC) and (2) oxygenated hydrocarbons. The concentrations reported here for NMOC were obtained by gas chromatographic methods for the identification and quantification of individual NMOC species (see Chapter 4). A fairly substantial data base exists for characterizing urban nonmethane hydrocarbon concentrations. Measurements of nonurban hydrocarbon levels, as well as both nonurban and urban oxygenated hydrocarbons, are much more limited. Among oxygenated hydrocarbons, aldehydes have received the most attention. Insufficient information exists for establishing ambient air concentrations of other classes of oxygenated hydrocarbons such as alcohols, ketones, acids, and ethers.

3.5.2.1.1 Urban nonmethane hydrocarbon concentrations. Most of the data on ambient air concentrations of nonmethane hydrocarbons (NMHC) have been obtained during the 6:00 to 9:00 a.m. time period. Since urban hydrocarbon emissions peak during that period of the day and atmospheric dispersion is limited, these concentrations generally reflect maximum diurnal levels. Table 3-14 lists the mean and range of NMHC concentrations recorded in a number of urban areas throughout the United States. For most urban areas included in the table, a mean NMHC value between 400 and 900 ppb C was observed, though mean concentrations in some cities (e.g., Houston, Las Vegas, and Los Angeles) are in excess of 1000 ppb C. The data in Table 3-14 are not meant to serve as a comparison of NMHC levels in various cities but rather are shown to indicate the mean and range of concentrations that have been reported. Comparisons are invalid because of major differences in sample numbers, site classifications, and seasonal sampling periods. In many cases, the range of values reported in Table 3-14 might not reflect the true maximum and minimum concentrations that occur in a particular urban area. Most of the hydrocarbon sampling programs were of short duration (~1 month) and in some cases were not operated on a daily basis. For example, the relatively high mean values reported in Las Vegas are undoubtedly the result of the fact that ambient air samples were only analyzed for hydrocarbons on days when conditions were appropriate for oxidant formation. It is probably safe to assume, however, that NMHC levels during the 6:00 to 9:00 a.m. time period in major urban areas will usually exceed 50 ppb C but seldom surpass 10,000 ppb C.

Species in the C_2-C_{10} molecular-weight range dominate the hydrocarbon composition of urban atmospheres, with the alkanes generally constituting 50 to 60 percent of the hydrocarbon burden, aromatics 20 to 30 percent, and alkenes and acetylene making up the remaining 5 to 15 percent (Sexton and Westberg, 1984). The alkane fraction is usually dominated by species in the C_4-C_6 molecular-weight range. Predominant aromatics include benzene, toluene, ethylbenzene, and the xylenes. The most abundant alkenes are ethylene and propene. The studies cited in Table 3-14 provide information on the individual species of NMHC found in urban atmospheres.

3.5.2.1.2 Nonurban nonmethane hydrocarbon concentrations . Nonurban nonmethane hydrocarbon concentrations are generally one to two orders of magnitude lower than those measured in urban areas (Ferman, 1981; Sexton and Westberg, 1984). Concentrations of individual species seldom exceed 10 ppb C. Total hydrocarbon

TABLE 3-14. NONMETHANE HYDROCARBON CONCENTRATIONS
MEASURED BETWEEN 6:00 and 9:00 a.m. IN VARIOUS UNITED STATES CITIES

City (Date)	Mean NMHC concn., ppb C	Range	Reference
Atlanta (1981)	491	113 to 1677	Westberg and Lamb (1983)
Baltimore (1980)	659	51 to 2798	Sexton and Westberg (1984)
Boston (1980)	569	83 to 4750	Sexton and Westberg (1984)
Cincinnati (1981)	840	260 to 1870	Holdren et al. (1982)
Detroit (1981)	330	60 to 1720	Kelly et al. (1986)
Houston (1976)	1414	356 to 16,350	Sexton and Westberg (1984)
Houston (1978)	1679	400 to 4500	Lonneman (1979)
Las Vegas (1980)	2506	689 to 4515	Naylor et al. (1981)
Las Vegas (1983)	2762	1835 to 4590	Naylor et al. (1984)
Los Angeles (1968)	3388	N.A.[a]	Lonneman (1977)
Los Angeles (1982)	2920	390 to 6430	Grosjean and Fung (1984)
Milwaukee (1981)	324	24 to 3116	Sexton and Westberg (1984)
Newark (1980)	732	89 to 6946	Sexton and Westberg (1984)
New York (1969)	830	N.A.	Lonneman (1977)
Philadelphia (1979)	669	305 to 1710	Sexton and Westberg (1984)
St. Louis (1973)	817	N.A.	Lonneman (1977)
Tulsa	426	103 to 3684	Eaton et al. (1979)
Washington, DC (1980)	671	210 to 2953	Sexton and Westberg (1984)

[a] Data are not available.

concentrations range up to ~150 ppb C, but usually fall in the range of about 5 to 100 ppb C. Alkanes comprise the bulk of species present, with C_2-C_5 compounds most abundant. Ethylene and propene are occasionally reported at concentrations of 1 ppb C or less, and toluene is usually present at ~1 ppb C.

Table 3-15 provides a summary of the range of hydrocarbon concentrations measured at various nonurban locations in the United States. Samples were carefully selected at most of the sites in order to guarantee their nonurban character. At the coastal and near-coastal sites, only those samples collected upwind of manmade sources (onshore advection) were included. The nonmethane

TABLE 3-15. NONMETHANE HYDROCARBON CONCENTRATIONS MEASURED IN NONURBAN ATMOSPHERES

Location	Species analyzed	Concentration range, ppb C	Reference
Belfast, ME	$C_2 - C_5$	10 to 22	Sexton and Westberg (1984)
Benicia, CA	$C_2 - C_5$	7 to 14	Sexton and Westberg (1984)
Miami, FL	$C_2 - C_5$	2 to 23	Sexton and Westberg (1984)
Glascow, IL	$C_2 - C_{10}$	60 to 150	Chatfield and Rasmussen (1977)
Janesville, WI	$C_2 - C_{10}$	9 to 24	Sexton and Westberg (1984)
Houston, TX	$C_2 - C_{10}$	2 to 24	Sexton and Westberg (1984)
Robinson, IL	$C_2 - C_{10}$	13 to 113	Sexton and Westberg (1984)
Smoky Mtns., TN	$C_2 - C_{10}$	38 to 149	Cronn (1982)
Northern Idaho	Terpenes	0.1 to 18	Holdren et al. (1979)
Virginia	Isoprene	4 to 150	Ferman (1981)
Atlanta (urban)	Isoprene	0 to 8	Westberg and Lamb (1983)
Whiteface Mtn., NY	Terpenes	6 to 84	Whitby and Coffey (1977)
Elkton, MO	Isoprene	0 to 28	Rasmussen et al. (1976)
Eastern TX	α-pinene	0.1 to 8	Seila (1981)
North Carolina	α-pinene	0.6 to 13	Seila (1981)
Colorado	Terpenes	0 to 8	Roberts et al. (1983)

hydrocarbon concentrations reported at coastal sites (Belfast, Benicia, Miami, and Houston) are definitely lower than those measured at most of the inland sites. It should be pointed out, however, that the numbers of samples measured for each of the nonurban locations listed in Table 3-15 is small. This, coupled with the fact that only a limited range of hydrocarbons were monitored in some cases, makes intersite comparisons tenuous at best.

Ambient air concentrations of naturally emitted hydrocarbons (e.g., isoprene, α-pinene, β-pinene, Δ-carene, and limonene) are generally reported only in nonurban hydrocarbon sampling programs. Because they are present at very low concentrations, natural hydrocarbons are extremely difficult to identify unequivocally when they mix with manmade emissions in an urban area. The one exception is isoprene, which has been reported in both urban and nonurban sampling programs. Monoterpene ($C_{10}H_{16}$) concentrations in ambient air seldom exceed 20 ppb C. Average concentrations of α-pinene, the most commonly reported monoterpene, are usually below 10 ppb C. During the summer months, isoprene concentrations as high as 150 ppb C have been measured (Ferman, 1981), but maximum concentrations in the 30 to 40 ppb C range are more common. Ambient concentrations of the naturally emitted hydrocarbons are site-dependent, with the highest concentrations observed in or immediately adjacent to forested areas. Concentrations vary with season, as well, because natural hydrocarbon emission fluxes are directly related to the amount of biomass present and increase with temperature. In a recent review article, Altshuller (1983) has provided a more detailed discussion of natural hydrocarbons and their effect on air quality.

3.5.2.2 Concentrations of Nitrogen Oxides in Ambient Air. Ambient air levels of nitrogen oxides have been monitored throughout the United States for a number of years. Since nitrogen dioxide (NO_2) is the only oxide of nitrogen for which an NAAQS has been promulgated, it has received the greatest attention. The emphasis here is on NO_x measurements that can be related to the diurnal photochemical processes that produce ozone.

3.5.2.2.1 Urban NO_x concentrations. Concentrations of NO_x, like hydrocarbon concentrations, tend to peak in urban areas during the early morning period when atmospheric dispersion is limited and automobile traffic is dense. Most of the NO_x is emitted as nitric oxide (NO), but the NO is converted rapidly to NO_2 by ozone and peroxy radicals produced in atmospheric photochemical reactions. Since ozone levels and photochemical activity vary diurnally and from day to day, the relative concentrations of NO and NO_2 can fluctuate significantly. Generally, urban NO concentrations peak during the 6:00 to 9:00 a.m. period, followed by a rapid decrease caused by the photochemical conversion of NO and NO_2 and increased atmosphere mixing. Nitric oxide levels remain low during the daytime and then usually build up again through the nighttime hours. Nitrogen dioxide concentrations typically increase during the mid-morning hours and then abate as the afternoon progresses. Levels of NO_2 increase again following the late afternoon rush-hour period, often continuing to increase during the nighttime.

The average NO_x concentration in urban areas of the United States is about 70 ppb, with NO and NO_2 contributing about equally (Logan, 1983). Monitoring data for 1975 through 1980 showed that peak 1-hr NO_2 concentrations equalled or exceeded 400 ppb in Los Angeles and several other California locations, as well as at sites in Kentucky (Ashland) and Michigan (Port Huron). Cities with one peak hourly concentration exceeding 270 ppb during those years include Phoenix; St. Louis; New York City; Springfield (Illinois); Cincinnati; Saginaw and Southfield (Michigan); and more than a dozen sites in California. Reported hourly concentrations in excess of 140 ppb were quite common nationwide during the years between 1975 and 1980 (U.S. Environmental Protection Agency, 1982a).

Urban NO_x concentrations during the 6:00 to 9:00 a.m. period are of primary importance in terms of oxidant production. Average NO_x levels recorded in several urban areas during this morning period are listed in Table 3-16, which shows mean 6:00 to 9:00 a.m. NO_x concentrations in the range of about 50 to 150 ppb. Concurrent 6:00 to 9:00 a.m. hydrocarbon samples were also obtained in the studies reported in Table 3-16, and the hydrocarbon-NO_x ratios in each of these urban areas are included.

TABLE 3-16. AVERAGE 6:00 to 9:00 a.m. NO_x CONCENTRATIONS AND HC/NO_x RATIOS IN URBAN AREAS

City	Average NO_x, ppb	Average HC/NO_x	References
Atlanta	57	9	Westberg and Lamb (1983)
Baltimore	85	10	Richter (1983)
Boston	63	10	Richter (1983)
Houston	125	13	Westberg et al. (1978b)
Detroit	67	5	Kelly et al. (1986)
Linden, NJ	59	16	Richter (1983)
Los Angeles	147	10	U.S. Environmental Protection Agency (1978a)
Milwaukee	66	5	Westberg and Lamb (1983)
St. Louis	77	8	U. S. Environmental Protection Agency (1978a)
Tulsa	46	13	Eaton et al. (1979)
Washington, DC	94	14	Richter (1983)

Hydrocarbon concentrations (ppb C) exceeded the NO_x levels by a factor of 5 to 16 during the 6:00 to 9:00 a.m. period. Smog chamber experiments indicate that significant quantities of ozone can be produced when HC/NO_x ratios are in this range. Indeed, ozone production has been observed in the vicinity of most of the cities referenced in Table 3-16.

3.5.2.2.2 Nonurban NO_x concentrations. Concentrations of NO_x in "clean" remote environments are usually below 0.5 ppb (Logan, 1983). For example, median concentrations measured on Niwot Ridge in Colorado are about 0.3 ppb in the summer and 0.24 ppb in winter. In exceptionally clean air, NO_x concentrations as low as 0.015 have been recorded (Bollinger et al., 1982). Slightly higher NO_x concentrations have been reported at other remote locations in the western United States and Canada. Kelly et al. (1982) deduced a mean NO_x concentration of about 1 ppb from measurements in South Dakota. At the South Dakota site, nitric oxide generally contributed less than 20 percent of the total NO_x. Measurements of NO_x during the 1970s at rural locations in Montana (Decker et al., 1978) and Saskatchewan (McElroy and Kerr, 1977) yielded average concentrations similar to those recorded in South Dakota.

At a rural site in Louisiana, Kelly et al. (1984) found mean concentrations of ~1 ppb NO and ~4 ppb NO_2. The same investigators observed mean concentrations of ~0.7 ppb NO and ~1.6 ppb NO_2 at a rural site in Virginia (Kelly et al., 1984).

In the northeastern United States, nonurban NO_x concentrations appear to exceed those in the west by about a factor of ten. A median NO_x concentration of 6.6 ppb was derived from data collected at nine rural sites utilized in the Sulfate Regional Experiment (SURE) program (Mueller and Hidy, 1983). Median concentrations at the individual stations, which extended eastward from the Ohio River Valley to the Atlantic Coast, varied from 2 to 11 ppb. Measurements at nonurban sites in Pennsylvania and Louisiana during the summer of 1975 showed mean hourly NO_x concentrations of 4.7 and 4.1 ppb, respectively (Decker et al., 1978). Nitric oxide composed approximately 40 percent of the total NO_x at these latter two nonurban sites.

3.6 SOURCE-RECEPTOR (OXIDANT-PRECURSOR) MODELS

In order to apply knowledge of the atmospheric chemistry of ozone and other photochemical oxidants and their precursors during their dispersion and transport, models describing these phenomena have been developed in a variety of forms over the past 15 years. Most of these models relate the rates of precursor emissions from mobile and stationary sources, or precursor atmospheric concentrations, to the resulting ambient concentrations of secondary pollutants that impact receptors at downwind sites. For this reason they have been described as source-receptor or oxidant-precursor models.

A wide variety of source-receptor models exists, ranging in complexity from empirical relationships based on air monitoring or smog chamber data to complex computer-based grid or trajectory airshed models that may contain detailed emission inventories, sophisticated dispersion and transport submodels, and lengthy chemical reaction mechanisms. Moving-box models represent an approach of intermediate complexity.

All presently available source-receptor models require a degree of simplifying assumptions to deal with practical limitations imposed by existing computer capabilities, time and cost constraints, or lack of knowledge concerning inputs such as boundary conditions, emissions, wind fields, or detailed reaction mechanisms. The reliability and applicability of any particular model therefore depend upon its specific limitations, data requirements, and degree of validation against experimental data from ambient air measurements or environmental chamber runs.

A detailed discussion of the range of available source-receptor models, and their validation and applications, is beyond the scope of this document. Instead, brief conceptual descriptions are provided of the major classes of source-receptor models. It is important to recognize that such models are continually undergoing evolution, revision, and refinement, particularly as knowledge of atmospheric chemistry grows and, for example, as more sophisticated approaches to dealing with boundary conditions become available. Even under the best circumstances, however, the present generation of source-receptor models should be viewed as being most useful for investigating the relative effects on air quality of particular emission sources or emission control strategies, rather than for predicting absolute concentrations of secondary pollutants resulting from specific precursor emissions.

3.6.1 Definitions, Descriptions, and Use

Current air-quality, or source-receptor, models can be classified as either statistical or computational/dynamic. Statistical models are generally based on an analysis of historical air quality data. An example of a statistical model is the linear rollback concept.

Computational, or dynamic, models attempt to describe mathematically the atmospheric chemical and physical processes influencing air pollution formation and impacts. Examples of computational models include trajectory and grid airshed models. The basis of these models is the solution of the atmospheric diffusion equation (Bird et al., 1960; Liu and Seinfeld, 1975).

Two phenomenologically different approaches have been employed in dynamic models with respect to the coordinate systems chosen. A coordinate system fixed with respect to the earth is termed Eulerian, while in Lagrangian models the reference frame moves with the air parcel whose behavior is being simulated.

In the following section these and other models are briefly described.

3.6.1.1 Statistical Models. Two widely used models of this kind are linear rollback and the Appendix J approach, both of which were employed by EPA prior to the advent of more sophisticated dynamic modeling approaches. The concept of linear rollback is based on the assumption that ambient concentrations of air pollutants are directly proportional to emissions; and that a given reduction in emissions will result in a proportional decrease in the maximum ambient concentrations of that pollutant. In principle, linear rollback models should be applied only to inert primary pollutants and their original use was for unreactive pollutants such as carbon monoxide (Larsen, 1969). Such models have been applied, however, in modified form to secondary pollutants such as ozone (Barth, 1970).

A prominent example of a statistical model was the Appendix J relationship developed by EPA to relate maximum 1-hour average ozone concentrations in several United States cities to 6:00-to-9:00 a.m. average nonmethane hydrocarbon concentrations in those cities (F.R., 1971). This relationship was used to calculate the amount of NMHC control needed to achieve the Federal standard for photochemical oxidants.

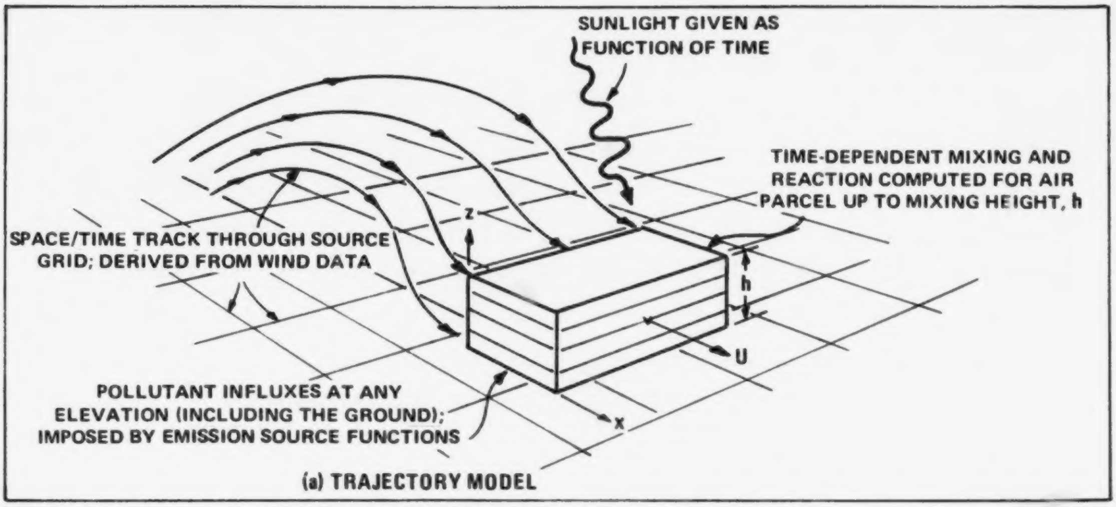
Two important limitations of past statistical methods were their failure to take into account the transport of primary and secondary pollutants from source areas to downwind receptor sites, and lack of recognition of the role of oxides of nitrogen in the formation of ozone and other photochemical oxidants.

These and other weaknesses led EPA to abandon the use of statistical models in state implementation plans (F.R., 1981).

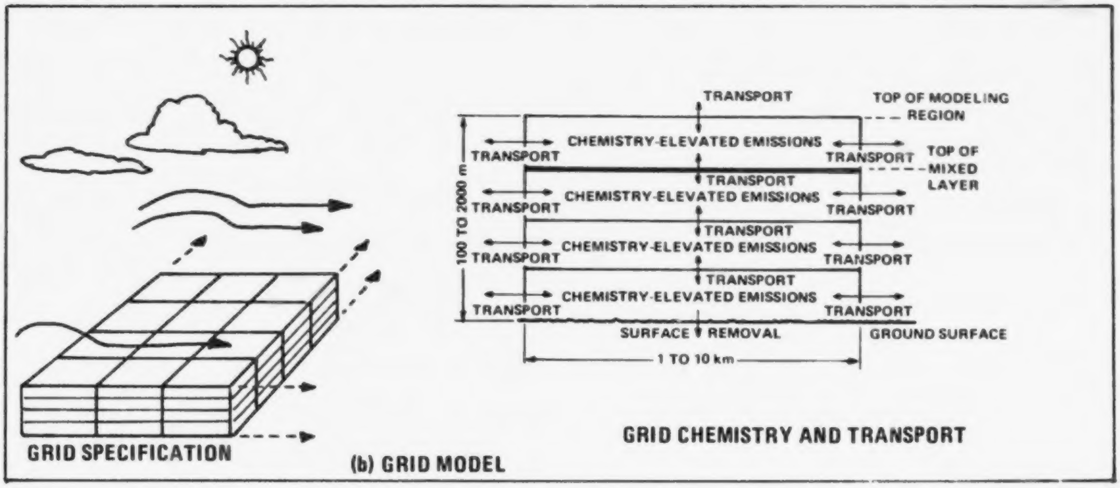
3.6.1.2 Trajectory Models. Figure 3-17(a) contains a schematic representation of the trajectory model approach, in which a hypothetical air parcel moves through the area of interest along a path calculated from wind trajectories. Thus, a moving-coordinate system (Lagrangian) describes pollutant transport under the influence of local meteorological conditions. Emissions are injected into the air parcel and undergo vertical mixing and chemical transformations.

The data requirements for trajectory models include: (1) initial concentrations of all relevant pollutants and species; (2) rates of emissions of NMOC and NO_x precursors into the parcel along its trajectory; (3) meteorological characteristics such as wind speed and direction; and (4) solar ultraviolet radiation. Various trajectory models exhibit a range of sophistication and complexity with regard to such elements as chemical mechanisms (Atkinson et al., 1982c), emission inventories (Braverman and Layland, 1982), treatment of vertical mixing (Whitten and Hogo, 1978; Drivas, 1977; Meyers et al., 1979; Lloyd et al., 1979; Lurmann et al., 1979), and trajectory determination (U.S. Environmental Protection Agency, 1980c; Whitten and Hogo, 1978). Basic limitations of trajectory models include the amount and density of data required for precise calculations of emissions input, chemical transformations, and dilution; neglect of horizontal wind shear; neglect of cell volume changes resulting from convergence and divergence of the wind field; and uncertainties in boundary conditions, including conditions aloft (Liu and Seinfeld, 1975). Conversely, moving-cell models provide a dynamic description of atmospheric source-receptor relationships that is simpler and less expensive to derive than that obtained from fixed-cell models.

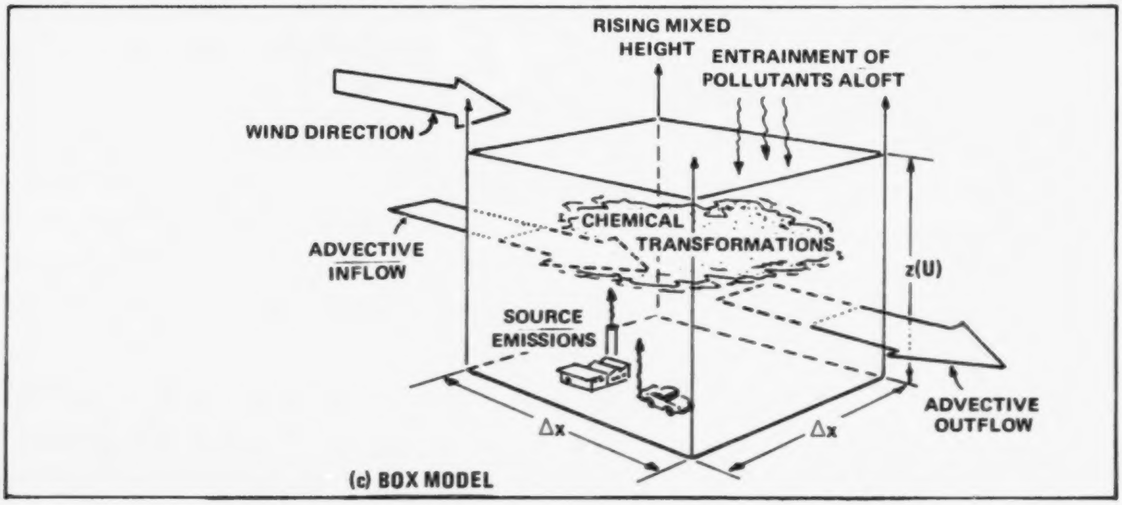
The simplest form of trajectory model is the empirical kinetic modeling approach (EKMA). This modeling approach was developed from earlier efforts (Dimitriades, 1972) to use smog chamber data to develop graphical relationships between morning NMOC and NO_x levels and afternoon ozone maximum concentrations. Dodge (1977a,b) presented an approach in which smog chamber data (Dimitriades, 1970; 1972) were used to test and validate a photochemical kinetics model (Durbin et al., 1975). Dimitriades (1977) used the resulting O_3 isopleths to define a method for obtaining the relative degree of precursor emissions control needed to achieve a given percentage reduction in ozone. In the EKMA approach, which has been extensively utilized (U.S. Environmental Protection


SUNLIGHT GIVEN AS FUNCTION OF TIME
TIME-DEPENDENT MIXING AND REACTION COMPUTED FOR AIR PARCEL UP TO MIXING HEIGHT, h
z
h
U
x
SPACE/TIME TRACK THROUGH SOURCE GRID; DERIVED FROM WIND DATA
POLLUTANT INFLUXES AT ANY ELEVATION (INCLUDING THE GROUND); IMPOSED BY EMISSION SOURCE FUNCTIONS

(a) TRAJECTORY MODEL


GRID SPECIFICATION
TRANSPORT
TOP OF MODELING REGION
CHEMISTRY-ELEVATED EMISSIONS
TRANSPORT
TRANSPORT
TOP OF MIXED LAYER
TRANSPORT
CHEMISTRY-ELEVATED EMISSIONS
TRANSPORT
TRANSPORT
TRANSPORT
CHEMISTRY-ELEVATED EMISSIONS
TRANSPORT
TRANSPORT
TRANSPORT
CHEMISTRY-ELEVATED EMISSIONS
TRANSPORT
TRANSPORT
100 TO 2000 m
SURFACE REMOVAL
GROUND SURFACE
1 TO 10 km
GRID CHEMISTRY AND TRANSPORT

(b) GRID MODEL


RISING MIXED HEIGHT
ENTRAINMENT OF POLLUTANTS ALOFT
WIND DIRECTION
CHEMICAL TRANSFORMATIONS
ADVECTIVE INFLOW
z(U)
SOURCE EMISSIONS
ADVECTIVE OUTFLOW
Δx
Δx

(c) BOX MODEL

Figure 3-17. Schematics of the three types of dynamic models.

Agency, 1978a,b; 1980c), the Ozone Isopleth Plotting Package (OZIPP) (Whitten and Hogo, 1978) is used to generate ozone isopleths at various levels of sophistication corresponding to "standard" EKMA, "city-specific" EKMA, or the "simplified trajectory" model (F.R., 1979). These models are designated as Levels IV, III, and II, respectively, with Level IV being the least sophisticated and Level II the most sophisticated. Substantial documentation and guidance concerning the use of OZIPP and a more flexible modified version of the Program (OZIPM) are available (U.S. Environmental Protection Agency, 1981a, 1984b,c).

The sensitivity of this method to variables such as the input hydrocarbon composition and the choice of chemical kinetics mechanisms has been reported (Carter et al., 1982; Jeffries et al., 1981; Shafer and Seinfeld, 1985) and further refinements in the EKMA approach to accomodate these factors have been made. For example, site-specific versions of EKMA allow the user to select particular dilution rates, emissions, and solar intensity applicable to the city or airshed of interest. Another version allows the user to employ an alternative mechanism for making the EKMA calculations (U.S. Environmental Protection Agency, 1984b).

Because it is often recommended by EPA for use in determining needed precursor reductions and is in widespread use, EKMA is discussed here in detail. An example of an EKMA diagram is presented in Figure 3-18, which shows ozone isopleths for sites downwind of an urban source area in which morning precursor emissions are high. The isopleths in this diagram depict downwind, peak 1-hour ozone concentrations as an explicit function of initial (i.e., morning) concentrations of nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x); and as indirect functions of (1) NMHC and NO_x emissions occurring later in the day; (2) specified meteorological conditions; (3) reactivity of the precursor mix; and (4) concentrations of ozone and precursors transported from upwind areas (U.S. Environmental Protection Agency, 1977). The relationships between ozone and its precursors that are depicted in Figure 3-18 are based on empirical data and the application of a chemical kinetics model (Dodge, 1977a; Whitten and Hogo, 1977) that has been adjusted by comparing model predictions against smog-chamber data obtained by irradiating automobile exhaust (Dimitriades, 1972). Alternatively, EKMA diagrams can be constructed using more recent chemical mechanisms that have been tested against smog chamber data (Gipson, 1984; Whitten and Gery, 1986).

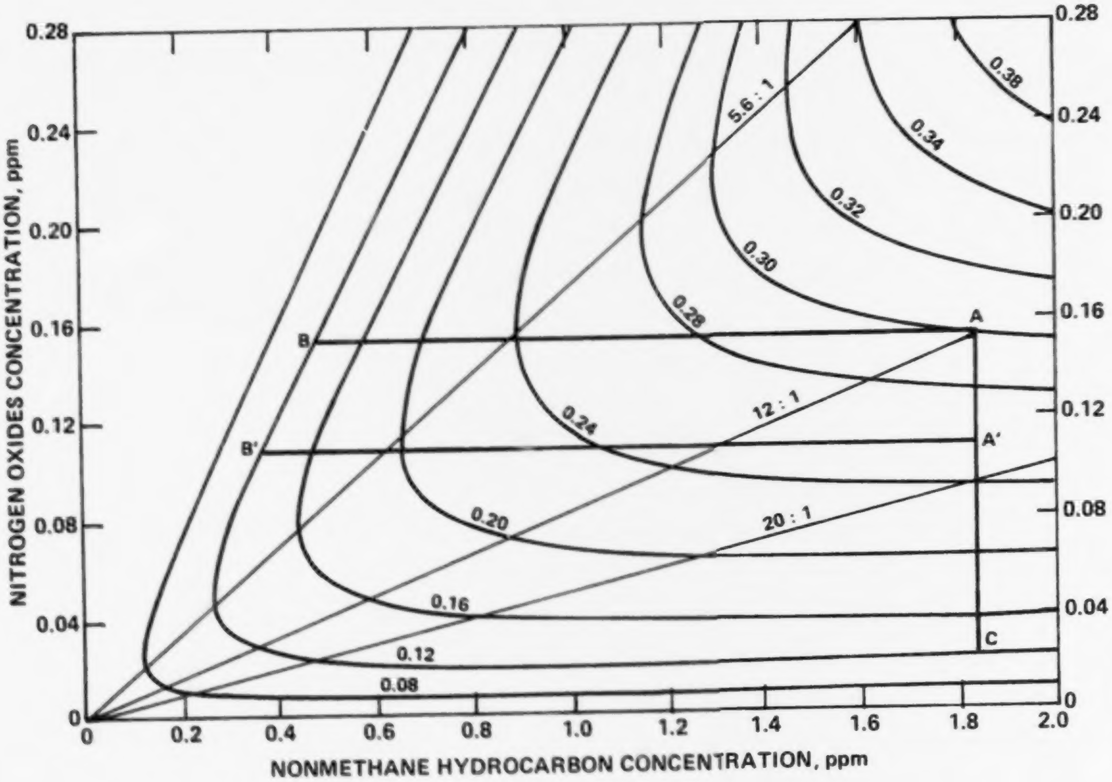


Figure 3-18 Example of EKMA diagram for high-oxidant urban area.

For the EKMA diagram given here as Figure 3-18, several general, interrelated features are of interest. First, the isopleth lines in the lower right quadrant are more or less parallel to the abscissa (the NMHC concentration). Second, the isopleth lines in the upper left quadrant are slanted with respect to the ordinate (the NO_x concentration). Because of the shape of the isopleth lines, varying the NMOC or NO_x concentration will have different effects on ozone at different NMHC/NO_x ratios.

These two features of the diagram are related to the underlying photochemistry (see, e.g., Whitten, 1983). For extremely low NO_x concentrations (i.e., high NMHC/NO_x ratios), where the lines parallel the abscissa, the formation of O_3 is (1) insensitive to changes in NMHC concentrations, and (2) NO_x-limited; that is, changes in NO_x concentrations cause co-directional changes in peak O_3 concentrations. As described early in Section 3.3 and in Section 3.3.1, the atmospheric oxidation of hydrocarbons produces an abundance of peroxy radicals ($RO_2\cdot$), more than enough to oxidize NO to NO_2 rapidly and completely. In addition, the NO_x present, before being removed from the cyclic reactions via termination reactions with various radicals, completes a number of $NO \xrightarrow{RO_2\cdot} NO_2 \longrightarrow NO\ (+\ O_3)$ cycles, thus producing a number of O_3 molecules. Small-to-moderate changes in NMHC concentrations will therefore have little impact, since there will still be an abundance of $RO_2\cdot$ radicals in the atmosphere. On the other hand, changing the already low concentration of NO_x does not have an appreciable impact on the RO_2 radicals, but it does change co-directionally the number of O_3 molecules produced, since the photolysis of NO_2 and the oxidation of NO to NO_x are essential for O_3 production.

For moderately higher concentrations of NO_x (lower NMHC/NO_x ratios), there is no longer a large abundance of $RO_2\cdot$ relative to the NO present; and changes in NMHC, therefore, have a co-directional effect on $RO_2\cdot$ and, hence,on O_3. Thus, for moderate NMHC/NO_x ratios, the effects on O_3 formation of varying the concentrations of NMHC or NO_x are similar in direction.

Finally, for much higher NO_x concentrations (i.e., very low NMHC/NO_x ratios), the dominant effects are the relative depletion of radicals, through the reactions of NO_2 with these radicals (Equations 3-18 and 3-35, Section 3.3); with a resulting decrease in the rate of reaction of peroxy radicals with NO (Equation 3-29, Section 3.3). The consequence of these effects is that the conversion of NO to NO_2 is very slow. At such low NMHC/NO_x ratios, therefore, increasing the NMHC concentration enhances O_3 formation but increasing NO_x concentrations inhibits it.

As examination of Figure 3-18 reveals, for an NMHC concentration of 0.6 ppm C, for example, increasing NO_x leads to increased O_3 until NMHC/NO_x ratios of about 5:1 to 6:1 are reached; further NO_x increases, leading to lower NMHC/NO_x ratios, inhibit O_3 formation. Thus, in this example, there is a "critical" ratio (approximately 5.6:1) at which the NO_x effect on O_3 changes direction. Besides this "critical" ratio, an "equal control" NMHC/NO_x ratio also exists, above which the reduction of NO_x is more beneficial in terms of O_3 reduction than an equal percentage reduction in NMHC. This ratio, for the isopleths shown in Figure 3-18, is roughly 8:1 to 9:1 for low levels of control, and as high as 20:1 for the levels of control needed to reduce O_3 to 0.12 ppm. Thus, for this particular case (Figure 3-18), the chemical mechanism modeling evidence suggests that (1) NO_x control will increase the peak downwind O_3 concentration at NMHC/NO_x ratios of 5.6:1 or lower; (2) both NO_x control and NMHC control will be beneficial at somewhat higher ratios, with control of NMHC being more effective; and (3) for ratios above 20:1, NO_x control is relatively more effective in reducing O_3.

The calculation of precursor controls necessary to reduce O_3 to 0.12 ppm, from the isopleths given in Figure 3-18, shows that NO_x control, although at first beneficial, is ultimately detrimental because it makes the reduction of O_3 to 0.12 ppm more difficult. This can be demonstrated through use of the EKMA isopleths in Figure 3-18 as follows. For a high-oxidant atmosphere with, for example, a peak O_3 concentration of 0.30 ppm and an NMHC/NO_x ratio of 12:1, a 74 percent control of NMHC (1.84 ppm C to 0.48 ppm C) will be needed in order to reduce downwind, 1-hour peak O_3 to 0.12 ppm through the unilateral control of NMHC (line AB in Figure 3-18). If, however, NO_x is first controlled by, for example, 29 percent (from 0.152 ppm to 0.108 ppm, line AA'), this will cause a 15 percent reduction in O_3 (line AA') but it will also increase the NMHC control requirement (to reduce O_3 to 0.12 ppm) from 74 percent (line AB) to 81 percent (line A'B'). Since it is not ordinarily feasible to reduce O_3 to 0.12 ppm in a high-oxidant area through the unilateral control of NO_x (it would take, in this case, an almost 85 percent control of NO_x, line AC), it follows that 29 percent control (or any control) of NO_x, would ultimately be detrimental for the situation represented by these isopleths. There may be situations, however, in which the control of NO_x will not increase the NMHC control required to achieve a given percentage reduction in ozone. It must be emphasized that the preceding discussion of the implications of controlling VOC and NO_x is not applicable to all situations. These diagrams may differ when different chemical mechanisms or other model input data are used. Furthermore, conclusions drawn from Figure 3-18 may differ if a different starting point on the diagram is used.

As noted early in Section 3.3, the effects on O_3 formation of controlling NO_x emissions are a matter of continuing discussion and research. The inhibition of O_3 formation by NO_x under some circumstances, as demonstrated by the EKMA diagram in Figure 3-18, has been shown in smog chamber studies (e.g., Glasson and Tuesday, 1970; Dimitriades, 1972). In a more recent study, in which he irradiated ambient air in Teflon bags, Kelly (1985) showed that the addition of NO_x to the Detroit ambient air samples suppressed O_3 formation. Kelly also compared EKMA predictions with the results of his smog chamber study and concluded that EKMA correctly describes the respective effects of NO_x and NMHC (or NMOC, as reported in the study) on ozone maxima.

The studies cited above, as well as other documentation (e.g., Dimitriades, 1977; Liu and Grisinger, 1981; Chock et al., 1981; Kelly, 1985; and references therein), should be consulted for more complete discussions of the respective effects of NMHC and NO_x controls on resulting peak ozone concentrations.

3.6.1.3 Fixed-Grid Models. Fixed-grid models, also called regional airshed models, are based on two- or three-dimensional arrays of grid cells fixed with respect to the earth (Eulerian) and are the most sophisticated source-receptor models presently available. As indicated in Figure 3-15(b), these models take into consideration the transfer of pollutants between adjacent cells, in addition to accounting for emissions, atmospheric chemistry, vertical mixing, and meteorological parameters. Such models are computationally complex and require the most extensive set of input data, but they also provide the most realistic treatment of the various processes involved in photochemical air pollution formation.

Examples of grid models that have been applied to emission control strategies and their assessment include the Systems Applications, Inc., airshed model (Reynolds et al., 1979) and the Livermore Regional Air Quality (LIRAQ) model (MacCracken et al., 1978). These models are most often used to simulate days for which detailed aerometric data are available. The availability of such data depends upon the number and spacing of ground monitoring stations, the amount of data on wind and turbulence aloft, and the frequency of vertical soundings. Wind, temperature, inversion, and diffusivity data are interpolated over the field of interest as part of the process of preparing inputs for grid models (Roth et al., 1976). In addition to atmospheric data, various emissions sources must be considered in each model. At the most sophisticated level, emission models and inventories are constructed to provide estimates, by category, of vehicular, aircraft, power plant, refinery, and distributed source emission rates, including their temporal and seasonal variations (Roth et al., 1976; Braverman and Layland, 1982; F.R., 1979).

Shortcomings in grid models stem from the theoretical and computational complexities that are necessary in this type of simulation. Inaccuracies in grid-model predictions arise from: (1) theoretical deficiencies in the mathematical representation of atmospheric processes; (2) numerical inaccuracy in the solution of the atmospheric diffusion equation (Liu and Seinfeld, 1975); and (3) inadequate input data resulting from incomplete data bases. An incomplete understanding of advection and turbulent diffusion, necessitates the use of estimates or parameterizations to provide appropriate values (Seinfeld and Wilson, 1977). Atmospheric chemical kinetics descriptions are continually updated as new information is obtained, but uncertainties associated with these mechanisms may be propagated during solution. In addition, sparse and often unrepresentative data are utilized to derive continuous fields (wind fields, turbulence, and mixing depths) over the region (Seinfeld and Wilson, 1977), a problem that is common to all dynamic models. In general, wind and turbulence data are rarely collected aloft; surface data are much more abundant but still vary widely in terms of number, frequency, and quality of measurements (Roth et al., 1976). This implies that critical values, especially aloft, must often be estimated to provide initial, boundary, and operating conditions (Seinfeld and Wilson, 1977). Finally, uncertainty in grid-model solutions also arises from emission inventories that are poorly resolved, either spatially, temporally, or with respect to hydrocarbon reactivity specifications (Braverman and Layland, 1982).

The structure and complexity of grid models also account for their utility. The increased temporal resolution afforded by grid models can provide minute-by-minute concentration estimates in each cell, and there can be as much spatial resolution as the data will allow. Since it accounts for specific atmospheric processes within the system, the model allows explicit insertion of new information (e.g., on meteorological or chemical processes) into the structure of the model. In addition, the impact of individual precursor sources may be analyzed with this type of model (Association of Bay Area Governments, 1979a,b).

3.6.1.4 Box Models. Box models (Hanna, 1973; Demerjian and Schere, 1979; Derwent and Höv, 1980) are the simplest of dynamic models. They treat the atmosphere as a single cell, bounded by the mixing layer, with an area on the order of 100 square miles [see Figure 3-15(c)]. The chemistry within the box is affected by: (1) instantaneously mixed regional emissions, (2) dilution from lifting of the inversion, (3) ventilation and transport resulting from a characteristic wind field, and (4) entrainment of species from aloft. Because the only consideration of spatial resolution occurs when the modeling boundaries are chosen, data requirements are minimal. Results can only be interpreted temporally, however, for a mass average of a species, and results can be strongly affected by uncertainties in boundary conditions.

3.6.2 Validation and Sensitivity Analyses for Dynamic Models

Dynamic models are mathematical representations of atmospheric processes. They are based on many assumptions, however, and can only be considered approximations of real processes. Therefore, it is important to investigate the extent to which model predictions disagree with actual measurements. Deviations occur for two basic reasons: (1) a completely valid mathematical description of natural systems does not presently exist; and (2) input data and data for comparison with predictions are often unresolved and imprecise (Seinfeld and Wilson, 1977). It is therefore difficult to determine numerically the overall accuracy of model calculations. Rather, attempts are made to validate model predictions by comparing them with real observations and operating parameters are often varied to determine the sensitivity of the model (Gelinas and Vajk, 1979). In addition, the extent of agreement between the results from two simulations can be tested. In this way, completely different models may be compared, or an internal component, such as the chemical kinetics mechanism, may be substituted and a model re-run to ascertain the effects of such substitutions.

It should be noted that the validity of all dynamic models depends, in part, on the quality of the chemical kinetics mechanisms used to define the O_3-HC-NO_x relationship. These mechanisms have the advantage of being cause-and-effect descriptions derived from actual experimental data. The data are subject, however, to the effects of smog chamber artifacts (Carter et al., 1982), which may or may not occur in the atmosphere. Also, there remain substantial uncertainties in the detailed chemistry of certain classes of organics such as the aromatics (Section 3.3). In addition, only recently have data become available so that mechanisms can be tested against data bases in which the hydrocarbon composition has been systematically varied or in which dynamic dilution and injection of new reactants has occurred (Jeffries et al., 1981). Therefore, dynamic models using existing chemical mechanisms may not accurately describe all of the conditions that apply in the atmosphere (Jeffries et al., 1981).

Evaluations of complex dynamic models have been of two forms: numerical sensitivity analyses and simulation performance studies using ambient air data. Sensitivity analyses have considered the effects of varying meteorological factors, initial and boundary air quality data and emissions inputs, model structure and computational factors, and reactions within the chemical kinetics mechanism (U.S. Environmental Protection Agency, 1981g; Liu and Seinfeld, 1975; Gelinas and Vajk, 1979; Tilden and Seinfeld, 1982; Dunker, 1980, 1981; Falls et al., 1979).

A comparative study of the Photochemical Box Model (PBM) of Demerjian and Schere (1979), the Lagrangian Photochemical Model (LPM) developed by Lurmann et al. (1979), and the Urban Airshed Model (UAM) (Ames et al., 1978) was performed in which the models were compared in "off-the-shelf" use (Schere and Shreffler, 1982a,b). That is, no effort was made to adjust the model predictions, although great care was taken in preparation of data and in model execution. Based upon application of these models to St. Louis air quality data, a fourth model, LIRAQ, was shown to be unsatisfactory and was not evaluated further (Schere and Shreffler, 1982a,b).

The remaining three models yielded adequate source-receptor information, provided knowledgeable interpretation of the output was applied. For instance, the PBM averaged 23 percent overprediction of ozone concentration over all test days, but in the 5 stagnation days for which the maximum ozone observed occurred within the PBM domain the average overprediction was only 8 percent. The LPM showed the largest variance in the ozone concentration residuals, possibly because the input data were not precise enough to fulfill the temporal and spatial demands of the model. As in previous studies (Whitten and Hogo, 1981; Reynolds et al., 1982; Cole et al., 1982), the UAM predicted ozone maximum concentrations with little bias (about 4 percent overprediction), but had difficulty placing the "ozone cloud" at the correct time and place. Again, this suggests uncertainty in specifying the wind field data. The user of any of these models must have a strong scientific background and must exercise extreme care in implementing air quality simulations (Schere and Shreffler, 1982a,b).

Because of their wide use, Levels II, III, and IV of EKMA have been the subject of many evaluation efforts. These include parameter sensitivity studies, comparison between the various levels of the approach, and studies comparing EKMA with other dynamic models (Meyer et al., 1981).

Jeffries and coworkers (1981) evaluated the performance of EKMA Levels II and III using 10 days of data from the 1976 St. Louis Regional Air Pollution Study. To evaluate the effects of chemistry and meteorology inputs, four different chemical kinetics mechanisms and three methods of calculating mixing-height profiles were employed. The choice of mechanism, trajectory, and mixing-height profile proved to have a large effect on the prediction of absolute ozone levels. No one mechanism or mixing-height profile was superior, however, at producing the "best fit" over all days. When the EKMA procedure was used in a relative sense to estimate needed reductions in NMHC, results obtained were not consistent. Improvements needed in the simple trajectory model (Level III) were identified as: (1) improved chemical kinetics descriptions, (2) smoother and more defined trajectories, (3) better treatment of point sources, and (4) improved mixing-height profiles.

In another sensitivity study, standard and city-specific versions of EKMA were used to simulate 100 pre-selected test days (Maxwell and Martinez, 1982). A statistical analysis was performed to determine how accurately these models, using three different chemical mechanisms, could predict absolute ozone levels. As above (Jeffries et al., 1981), none of the models was a consistently good predictor of ozone and ozone levels were usually overpredicted by more than 20 percent.

Finally, all three levels of EKMA were compared on a limited number of test days with respect to: (1) level of EKMA, (2) chemical kinetics mechanisms, and (3) isopleth diagram entry parameters (Hayes and Hogo, 1982). Again it was found that substituting chemical mechanisms produced significant differences in the shape of the isopleth curves. Also, and partly because of this, EKMA predictions were found to be quite sensitive to low NMHC/NO_x precursor ratios. Precursor-ozone relationships derived for various levels of EKMA were not particularly different, nor did they appear to be sensitive to the choice of trajectory (for Level II analysis).

Studies comparing EKMA performance with that of more complex dynamic models have also been carried out (Whitten and Hogo, 1981; U.S. Environmental Protection Agency, 1981a). Input to the EKMA model was often generated by the comparison model so that specific features could be compared. In all studies, the most sensitive difference, in terms of absolute prediction of ozone levels, was found to be the choice of chemical mechanism. It was shown, however, that application of the EKMA produced precursor-ozone descriptions similar to those from the more complex models when the same chemical mechanism was used in each of the models. Finally, it should be noted that the non-linear relationships between O_3 and its precursors means that good model performance in replicating base case conditions does not ensure accurate emission control calculations. To address this problem, emission control estimates obtained with EKMA have been compared with trends and emission reduction estimates obtained with grid models (Meyer et al., 1981). Further information on the comparative performance of EKMA is found in Dimitriades and Dodge (1983).

Selection of a modeling approach for determining ozone concentrations that is acceptable and appropriate for given circumstances necessitates making many interrelated decisions. All models considered should be able, of course, to simulate the physical and chemical processes known or suspected to be important. Potential users must then weigh the advantages of greater credibility and capability against the disadvantages of greater cost, time, and personnel requirements (Association of Bay Area Governments, 1979a). In addition to the technical aspects of potential modeling approaches, specific selection constraints also include: (1) extent of data requirements; (2) costs of data collection, model implementation, and operation; (3) computer constraints; (4) personnel requirements; and (5) schedule constraints. These criteria are not independent of one another, and time spent defining a selection plan can result in substantial benefits throughout the modeling exercise.

3.7 SUMMARY

3.7.1 Descriptions and Properties of Ozone and Other Photochemical Oxidants

Ozone (O_3) and other photochemical oxidants occurring at low concentrations in ambient air, such as peroxyacetyl nitrate (PAN), hydrogen peroxide (H_2O_2), and formic acid (HCOOH), are characterized chiefly by their ability to remove electrons from, or to share electrons with, other molecules or ions (i.e., oxidation). The capability of a chemical species for oxidizing or reducing other chemical species is termed "redox potential" (positive or negative standard potential) and is expressed in volts. A reactive allotrope of oxygen that is only about one-tenth as soluble as oxygen in water, ozone has a standard potential of +2.07 volts in aqueous systems for the redox pair, O_3/H_2O (Weast, 1977). Hydrogen peroxide, which is highly soluble in water and other polar solvents, has a standard potential of +1.776 in the redox pair, H_2O_2/H_2O (Weast, 1977). No standard potential for peroxyacetyl nitrate in neutral or buffered aqueous systems, such as those that occur in biological systems, appears in the literature. In acidic solution (pH 5 to 6), PAN hydrolyzes fairly rapidly (Lee et al., 1983; Holdren et al., 1984); in alkaline solution it decomposes with the production of nitrite ion and molecular oxygen (Stephens, 1967; Nicksic et al., 1967). An important property of PAN, especially in the laboratory, is its thermal instability. Its explosiveness dictates its synthesis for experimental and calibration purposes by experienced personnel only.

Formic acid is formed as a stable product in photochemical air pollution. It has the structure of both an acid and an aldehyde and in concentrated form is a pungent-smelling, highly corrosive liquid.

The toxic effects of oxidants are attributable to their oxidizing ability. Their oxidizing properties also form the basis of several measurement techniques for O_3 and PAN. The calibration of ozone and PAN measurements, however, is achieved via their spectra in the ultraviolet and infrared regions, respectively. All three pollutants of most concern in this document (O_3, PAN, and H_2O_2) must be generated _in situ_ for the calibration of measurement techniques. For ozone and H_2O_2, generation of calibration gases is reasonably straightforward.

3.7.2 Nature of Precursors to Ozone and Other Photochemical Oxidants

Photochemical oxidants are products of atmospheric reactions involving volatile organic compounds (VOC) and oxides of nitrogen (NO_x), as well as hydroxyl (OH) and other radicals, oxygen, and sunlight (see, e.g., Demerjian et al., 1974; National Research Council, 1977a; U.S. Environmental Protection Agency, 1978a; Atkinson, 1985). The oxidants are largely secondary pollutants formed in the atmosphere from their precursors by processes that are a complex, nonlinear function of precursor emissions and meteorological factors.

The properties of organic compounds that are most relevant to their role as precursors to ozone and other oxidants are their volatility, which governs their emissions into the atmosphere; and their chemical reactivity, which determines their lifetime in the atmosphere. Although vapor-phase hydrocarbons (compounds of carbon and hydrogen only) are the predominant organic compounds in ambient air that serve as precursors to photochemical oxidants, other volatile organic compounds are also photochemically reactive in those atmospheric processes that give rise to oxidants. In particular, halogenated organics (e.g., haloalkenes) that participate in photochemical reactions are present in ambient air, although at lower concentrations than the hydrocarbons. They are oxidized through the same initial step involved in the oxidation of the hydrocarbons; that is, attack by hydroxyl radicals. Alkenes, haloalkenes, and aliphatic aldehydes are, as classes, among the most reactive organic compounds found in ambient air (e.g., Altshuller and Bufalini, 1971; Darnall et al., 1976; Pitts et al., 1977; U.S. Environmental Protection Agency, 1978a, and references therein). Alkenes and haloalkenes are unique among VOC in ambient air in that they are susceptible both to attack by OH radicals (OH) and by ozone (Niki et al., 1983). Methane, halomethanes, and certain haloethenes are of negligible reactivity in ambient air and have been classed as unreactive by the U.S. Environmental Protection Agency (1980a,b). Since methane is considered only negligibly reactive in ambient air, the volatile organic compounds of importance as oxidant precursors are usually referred to as nonmethane hydrocarbons (NMHC) or, more properly, as nonmethane organic compounds (NMOC).

The oxides of nitrogen that are important as precursors to ozone and other photochemical oxidants are nitrogen dioxide (NO_2) and nitric oxide (NO). Nitrogen dioxide is itself an oxidant that produces deleterious effects, which are the subject of a separate criteria document (U.S. Environmental Protection Agency, 1982a). Nitrogen dioxide is an important precursor (1) because its photolysis in ambient air leads to the formation of oxygen atoms that combine with molecular oxygen to form ozone; and (2) because it reacts with acetylperoxy radicals to form peroxyacetyl nitrate, a phytotoxicant and a lachrymator. Although ubiquitous, nitrous oxide (N_2O) is unimportant in the production of oxidants in ambient air because it is virtually inert in the troposphere.

3.7.3 Atmospheric Reactions of Ozone and Other Oxidants Including Their Role in Aerosol Formation

The chemistry of the polluted atmosphere is exceedingly complex, but an understanding of the basic phenomena is not difficult to acquire. Three processes occur: the emission of precursors to ozone from predominantly manmade sources; photochemical reactions that take place during the dispersion and transport of these precursors; and scavenging processes that reduce the concentrations of both O_3 and precursors along the trajectory.

The specific atmospheric reactions of ozone and of other photochemical oxidants such as peroxyacetyl nitrate and hydrogen peroxide are becoming increasingly well-characterized. The reactions of these species result in products and processes that may have significant environmental and health- and welfare-related implications, including effects on biological systems, nonbiological materials, and such phenomena as visibility degradation and acidification of cloud and rain water.

3.7.3.1 Formation and Transformation of Ozone and Other Photochemical Oxidants. In the troposphere, ozone is formed through the dissociation of NO_2 by sunlight to yield an oxygen atom, which then reacts with molecular oxygen (O_2) to produce an O_3 molecule. If it is present, NO can react rapidly with O_3 to form NO_2 and an O_2 molecule. In the absence of competing reactions, a steady-state or equilibrium concentration of O_3 is soon established between O_3, NO_2, and NO (National Research Council, 1977a). The injection of organic compounds into the atmosphere upsets the equilibrium and allows the ozone to accumulate at higher than steady-state concentrations. The length of the induction period before the accumulation of O_3 begins depends heavily on the initial NO/NO_2 and $NMOC/NO_x$ ratios (National Research Council, 1977a).

The major role played by organic compounds in smog reactions is attributable to the hydroxyl radical (OH), since it reacts with essentially all organic compounds (e.g., Atkinson, 1985; Herron and Huie, 1977, 1978; Dodge and Arnts, 1979; Niki et al., 1981). Aldehydes, which are constituents of automobile exhaust as well as decomposition products of most atmospheric photochemical reactions involving hydrocarbons, and nitrous acid (HONO), are important sources of OH radicals, as is O_3 itself. Other free radicals, such as hydro- and alkylperoxy radicals and the nitrate (NO_3) radical play important roles in photochemical air pollution.

The presence of organic compounds, oxides of nitrogen, and sunlight does not mean that the photochemical reactions will continue indefinitely. Termination reactions gradually remove NO_2 from the reaction mixtures, such that the photochemical cycles slowly come to an end unless fresh NO and NO_2 emissions are injected into the atmosphere. Compounds containing nitrogen, such as PAN, nitric acid (HNO_3), and peroxynitric acid (HNO_4), as well as organic and inorganic nitrates, are formed in these termination reactions.

Recent studies on the photooxidation of organic compounds under simulated atmospheric conditions have been reasonably successful. The rate constants for the reaction of OH radicals with a large number of organic compounds have been measured (e.g., Atkinson et al., 1979; Atkinson et al., 1985). The mechanisms of the reactions of paraffinic compounds are fairly well understood, as are those of olefinic compounds, at least for the smaller compounds. Photooxidation reactions of the aromatic compounds, however, are poorly understood.

In the presence of NO_x, natural hydrocarbons (i.e., those organic compounds emitted from vegetation) can also undergo photooxidation reactions to yield O_3, although most naturally emitted hydrocarbons are olefins and are scavengers as well as producers of O_3 (e.g., Lloyd et al., 1983; Atkinson et al., 1979; Kamens et al., 1982; Killus and Whitten, 1984; Atkinson and Carter, 1984).

3.7.3.2 Atmospheric Chemical Processes Involving Ozone. Ozone can react with organic compounds in the boundary layer of the troposphere (Atkinson and Carter, 1984). It is important to recognize, however, that organics undergo competing reactions with OH radicals in the daytime (Atkinson et al., 1979; Atkinson, 1985) and, in certain cases, with NO_3 radicals during the night (Japar and Niki, 1975; Carter et al., 1981a; Atkinson et al., 1984a,b,c,d,e; Winer et al., 1984), as well as photolysis, in the case of aldehydes and other oxygenated organics. Only for organics whose ozone reaction rate constants are greater than $\sim 10^{-21}$ cm^3 $molecule^{-1}$ sec^{-1} can consumption by ozone be considered to be atmospherically important (Atkinson and Carter, 1984).

Ozone reacts rapidly with the acyclic mono-, di-, and tri-alkenes and with cyclic alkenes. The rate constants for these reactions range from $\sim 10^{-18}$ to $\sim 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} (Atkinson and Carter, 1984), corresponding to atmospheric lifetimes ranging from a few minutes for the more reactive cyclic alkenes, such as the monoterpenes, to several days. In polluted atmospheres, a significant portion of the consumption of the more reactive alkenes will occur via reaction with ozone rather than with OH radicals, especially in the afternoons during photochemical oxidant episodes. Reactions between ozone and alkenes can result in aerosol formation (National Research Council, 1977a; Schuetzle and Rasmussen, 1978), with alkenes of higher carbon numbers the chief contributors.

Because of their respective rate constants, neither alkanes (Atkinson and Carter, 1984) nor alkynes (Atkinson and Aschmann, 1984) are expected to react with ozone in the atmosphere, since competing reactions with OH radicals have higher rate constants (Atkinson et al., 1979; Atkinson, 1985).

The aromatics react with ozone, but quite slowly (Atkinson and Carter, 1984), such that their reactions with ozone are expected to be unimportant in the atmosphere. Cresols are more reactive toward ozone than the aromatic hydrocarbons (Atkinson and Carter, 1984), but their reactions with OH radicals (Atkinson, 1985) or NO_3 radicals (Carter et al., 1981a; Atkinson et al., 1984d) predominate.

For oxygen-containing organic compounds, especially those without carbon-carbon double bonds, reactions with ozone are slow. For carbonyls and ethers (other than ketene) that contain unsaturated carbon-carbon bonds, however, much faster reactions are observed (Atkinson and Carter, 1984).

Certain reactions of ozone other than its reactions with organic compounds are important in the atmosphere. Ozone reacts rapidly with NO to form NO_2, and subsequently with NO_2 to produce the nitrate (NO_3) radical and an oxygen molecule. Photolysis of ozone can be a significant pathway for the formation of OH radicals, particularly in polluted atmospheres when ozone concentrations are at their peak.

Ozone may play a role in the oxidation of SO_2 to H_2SO_4, both indirectly in the gas phase (via formation of OH radicals and Criegee biradicals) and directly in aqueous droplets.

3.7.3.3 Atmospheric Reactions of PAN, H_2O_2, and HCOOH.

Because PAN is in equilibrium with acetyl peroxy radicals and NO_2, any process that leads to the removal of either of these species will lead to the decomposition of PAN. One such process is the reaction of NO with acetyl peroxy radicals. This can lead, however, to the formation of OH radicals. Thus, PAN remaining overnight from an episode on the previous day can react with NO emitted from morning traffic to produce OH radicals (Cox and Roffey, 1977; Carter et al., 1981c) that will enhance smog formation on that day (e.g., Tuazon et al., 1981a). In the absence of significant NO concentrations, and in regions of moderate to lower temperatures, PAN will persist in the atmosphere (Wallington et al., 1984; Aikin et al., 1983) and contribute to the long-range transport of NO_x.

Although hydrogen peroxide formed in the gas phase from the reactions of hydroperoxyl radicals plays a role in HO_x chemistry in the troposphere, and especially in the stratosphere (Crutzen and Fishman, 1977; Cox and Burrows, 1979), its major importance arises from its high solubility in water. The latter ensures that a large fraction of gaseous H_2O_2 will be taken up in aqueous droplets. Over the past decade, evidence has accumulated that H_2O_2 dissolved in cloud, fog, and rainwater may play an important, and, in acidic droplets (i.e., pH $\lesssim 5$), even a dominant role in the oxidation of SO_2 to H_2SO_4 (e.g., Hoffman and Edwards, 1975; Martin and Damschen, 1981; Chameides and Davis, 1982; Calvert and Stockwell, 1983, 1984; Schwartz, 1984). Hydrogen peroxide may also play a role in the oxidation of NO_2 dissolved in aqueous droplets, although relevant data are limited and additional research is required (see, e.g., Gertler et al., 1984). Substantial uncertainties remain concerning the quantitative role of H_2O_2 in acidification of aqueous particles and droplets (Richards et al., 1983).

Because it can be scavenged rapidly into water droplets, formic acid can potentially function as an oxidant in cloud water and rain water. Thus, HCOOH is an example of a compound that is a non-oxidant or weak oxidant in the gas phase but that is transformed upon incorporation in aqueous solutions into an effective oxidizer of S(IV). Although much uncertainty remains concerning the quantitative role of HCOOH and the higher organic acids, they potentially play a minor but still significant role in the acidification of rain.

3.7.4 Meteorological and Climatological Processes

Meteorological and climatological processes are important in determining the extent to which precursors to ozone and other photochemical oxidants can accumulate, and thereby the concentrations of ozone and other oxidants that can result. The meteorological factors most important in the formation and transport of ozone and other photochemical oxidants in the lower troposphere are: (1) degree of atmospheric stability; (2) wind speed and direction; (3) intensity and wavelength of sunlight; and (4) synoptic weather conditions. These factors are in turn dependent upon or interrelated with geographic, seasonal, and other climatological factors.

Incursions of ozone from the stratosphere are an additional source of the ozone found in the lower troposphere. The physical and meteorological mechanisms by which ozone is brought into the troposphere from the stratosphere are important in determining the resulting ground-level concentrations, ground-level locations impacted, and the seasonality of incursions of stratospheric ozone.

3.7.4.1 *Atmospheric Mixing*. The concentration of a pollutant in ambient air depends significantly on the degree of atmospheric mixing that occurs from the time the pollutant or its precursors are emitted and the arrival of the pollutant at the receptor. The rate at which atmospheric mixing proceeds and the extent of the final dilution depends on the amount of turbulent mixing that occurs and on wind speed and direction. Atmospheric stability is one of the chief determinants of turbulent mixing since pollutants do not spread rapidly within stable layers nor do they mix upward through stable layers to higher altitudes.

Temperature inversions, in which the temperature increases with increasing altitude, represent the most stable atmospheric conditions. Surface inversions (base at ground level) and elevated inversions (the entire layer is above the surface) are both common (Hosler, 1961; Holzworth, 1964) and both can occur simultaneously at the same location. Surface inversions show a diurnal pattern, forming at night in the absence of solar radiation but breaking up by about mid-morning as the result of surface heating by the sun (Hosler, 1961; Slade, 1968). Elevated inversions can persist throughout the day and pollutants can be trapped between the ground surface and the base of the inversion. The persistence of elevated inversions is a major meteorological factor contributing to high pollutant concentrations and photochemical smog conditions along the California coast (Hosler, 1961; Holzworth, 1964; Robinson, 1952). In coastal areas generally, such as the New England coast (Hosler, 1961) and along the Great Lakes (Lyons and Olsson, 1972), increased atmospheric stability (and diminished mixing) occurs in summer and fall as the result of the temperature differential between the water and the land mass.

The depth of the layer in which turbulent mixing can occur (i.e., the "mixing height") shows geographical dependence. Summer morning mixing heights are usually >300 m in the United States except for the Great Basin (part of Oregon, Idaho, Utah, Arizona, and most of Nevada), where the mixing height is ~200 m (Holzworth, 1972). By mid-morning, mixing heights increase markedly such that only a few coastal areas have mixing heights <1000 m.

Summer afternoon mixing heights are generally an indication of the potential for recurring photochemical oxidant problems. Photochemical smog problems in the United States are somewhat unexpected since the lowest afternoon mixing height is $\sim$600 m (Holzworth, 1972). Elevated inversions having bases $<$500 m (i.e., low-level inversions) occur in the United States, however, with the following frequencies: 90 percent on the California coast; $\gtrsim$20 percent on the Atlantic coast (New Jersey to Maine); $\gtrsim$5 percent along the Great Lakes; and 5 to 10 percent from Louisiana to Arkansas and eastward to about Atlanta, Georgia. For most areas of the United States, though, the persistence through the afternoon of low-level stable layers is a rare event, occurring on $<$1 day in 20 (Holzworth and Fisher, 1979).

3.7.4.2 Wind Speed and Direction. For areas in which mixing heights are not restrictive, wind speed and, in some cases, wind direction are major determinants of pollution potential. Since strong winds dilute precursors to ozone and other photochemical oxidants, a location may have good ventilation despite the occurrence of persistent inversions (e.g., San Francisco). Conversely, light winds can result in high oxidant levels even if the mixing layer is deep.

The frequency of weak winds, then, is important in oxidant formation. In industrialized, inland areas east of the Mississippi River, surface inversions in the morning coupled with wind speeds $\leq$2.5 m/sec ($\leq$6 mi/hr) occur with a frequency $\geq$50 percent (Holzworth and Fisher, 1979). These surface inversions break up by afternoon, however, permitting dispersion.

The effects of wind speed and direction include the amount of dilution occurring in the source areas, as well as along the trajectory followed by an urban or source-area plume. Regions having steady prevailing winds, such that a given air parcel can pass over a number of significant source areas, can develop significant levels of pollutants even in the absence of weather patterns that lead to the stagnation type of air pollution episodes. The Northeast states are highly susceptible to pollutant plume transport effects, although some notable stagnation episodes have also affected this area (e.g., Lynn et al., 1964). Along the Pacific Coast, especially along the coast of California, coastal winds and a persistent low inversion layer contribute to major pollutant buildups in urban source areas and downwind along the urban plume trajectory (Robinson, 1952; Neiburger et al., 1961).

3.7.4.3 Effects of Sunlight and Temperature. The effects of sunlight on photochemical oxidant formation, aside from the role of solar radiation in meteorological processes, are related to its intensity and its spectral distribution. Intensity varies diurnally, seasonally, and with latitude, but the effect of latitude is strong only in the winter. Experimental studies have verified the effects on oxidant formation of light intensity (Peterson, 1976; Demerjian et al., 1980) and its diurnal variations (Jeffries et al., 1975; 1976), as well as on the overall photooxidation process (Jaffee et al., 1974; Winer et al., 1979).

A correlation between high oxidant concentrations and warm, above-normal temperatures has been demonstrated generally (Bach, 1975; Wolff and Lioy, 1978) and for specific locations, e.g., St. Louis (Shreffler and Evans, 1982). Coincident meteorology appears to be the cause of the observed correlation. Certain synoptic weather conditions are favorable both for the occurrence of higher temperatures and for the formation of ozone and other oxidants, so that temperature is often used to forecast the potential for high oxidant concentrations (e.g., Wolff and Lioy, 1978; Shreffler and Evans, 1982). Data from smog chamber studies show an effect of temperature on ozone formation (e.g., Carter et al., 1979b; Countess et al., 1981), but the effect is thought to result from the volatilization and reaction of chamber wall contaminants as the temperature is increased.

3.7.4.4 Transport of Ozone and Other Oxidants and Their Precursors. The levels of ozone and other oxidants that will occur at a given receptor site downwind of a precursor source area depend upon many interrelated factors, which include but are not restricted to: (1) the concentrations of respective precursors leaving the source area; (2) induction time; (3) turbulent mixing; (4) wind speed and wind direction; (5) scavenging during transport; (6) injection of new emissions from source areas in the trajectory of the air mass; and (7) local and synoptic weather conditions.

Ozone and other photochemical oxidants can be transported hundreds of miles from the place of origin of their precursors, as documented by the numerous studies on transport phenomena that were described in the 1978 criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978a). In that document, transport phenomena were classified into three categories, depending upon transport distance: urban-scale, mesoscale, and synoptic-scale. In urban-scale transport, maximum concentrations of O_3 are produced about 20 miles or so (and about 2 to 3 hours) downwind from the major pollutant source areas. In mesoscale transport, O_3 has been observed up to 200 miles downwind from the sources of its precursors. Synoptic-scale transport is associated with large-scale, high-pressure air masses that may extend over and persist for many hundreds of miles.

Urban-scale transport has been identified as a significant, characteristic feature of the oxidant problem in the Los Angeles Basin (Tiao et al., 1975), as well as in San Franciso, New York, Houston, Phoenix, and St. Louis (e.g., Altshuller, 1975; Coffey and Stasiuk, 1975; Shreffler and Evans, 1982; Wolff et al., 1977a). Simple advection of a photochemically reactive air mass, local wind patterns, and diurnal wind cycles appear to be the main factors involved in urban-scale transport.

Mesoscale transport is in many respects an extension of urban-scale transport and is characterized by the development of urban plumes. Bell documented cases in 1959 in which precursors from the Los Angeles Basin and the resultant oxidant plume were transported over the coastal Pacific Ocean, producing elevated oxidant concentrations in San Diego County the next day (Bell, 1960). Similar scales of transport have been reported by Cleveland et al. (1976a,b) for the New York-Connecticut area; by Wolff and coworkers and others (Wolff et al., 1977a,c; Wolff and Lioy, 1978; Clark and Clarke, 1982; Clarke et al., 1982; Vaughan et al., 1982) for the Washington, DC-Boston corridor; and by Westberg and coworkers for the Chicago-Great Lakes area (Sexton and Westberg, 1980; Westberg et al., 1981). These and other studies have demonstrated that ozone-oxidant plumes from major urban areas can extend downwind about 100 to 200 miles and can have widths of tens of miles (Sexton, 1982), frequently up to half the length of the plume.

Synoptic-scale transport is characterized by the general and widespread occurrence of elevated oxidants and precursors on a regional or air-mass scale as the result of certain favorable weather conditions, notably, slow-moving, well-developed high-pressure, or anti-cyclonic, systems characterized by weak winds and limited vertical mixing (Korshover, 1967; 1975). The size of the region that can be affected has been described by Wolff and coworkers, who reported the occurrence of haze and elevated ozone levels in an area extending from the Midwest to the Gulf Coast (Wolff et al., 1982) and the occurrence of elevated ozone concentrations extending in a virtual "ozone river" from the

Gulf Coast to New England that affected anywhere from a few hundred square miles to a thousand square miles during a 1-week period in July 1977 (Wolff and Lioy, 1980).

3.7.4.5 Stratospheric-Tropospheric Ozone Exchange. The fact that ozone is formed in the stratosphere, mixed downward, and incorporated into the troposphere, where it forms a more or less uniformly mixed background concentration, has been known in various degrees of detail for many years (Junge, 1963). It is widely accepted that the long-term average tropospheric background concentration of about 30 ppb to 50 ppb results primarily, though not exclusively, from the transfer of stratospheric ozone into the upper troposphere, followed by subsequent dispersion throughout the troposphere (e.g., Kelly et al., 1982).

The exchange of ozone between the stratosphere and the troposphere in the middle latitudes occurs to a major extent in events called "tropopause folds" (TF) (Reiter, 1963; Reiter and Mahlman, 1965; Danielsen, 1968; Reiter, 1975; Danielsen and Mohnen, 1977; Danielsen, 1980), in which the polar jet stream plays a major role. From recent studies, Johnson and Viezee (1981) proposed four types or mechanisms of TF injection and concluded that two of these, both of which are consistent with theory, could cause substantial effects in terms of high ozone concentrations at ground level. They concluded, in addition, that all low-pressure trough systems may induce TF events and cause the trans-tropopause movement of ozone-rich air into the troposphere (Johnson and Viezee, 1981).

3.7.4.6 Stratospheric Ozone at Ground Level. From a detailed review of studies on background tropospheric ozone, Viezee and Singh (1982) concluded that the stratosphere is a major but not the sole source of background ozone in the unpolluted troposphere, a conclusion reached by other investigators as well (e.g., Kelly et al., 1982). The stratospheric ozone reservoir shows a strong seasonal cycle that is reflected at ground-level. At some stations that monitor background ozone levels, average spring background levels may be as high as 80 ppb, with average fall levels ranging from 20 to 40 ppb (e.g., Singh et al., 1977; Mohnen, 1977; U.S. Environmental Protection Agency, 1978a). Viezee and Singh (1982) and Viezee et al. (1983) concluded that relatively high ozone concentrations can occur for short periods of time (minutes to a few hours) over local areas as a result of stratospheric intrusions.

A number of investigators have attempted to quantify the amount of the surface ozone that can be attributed to stratospheric sources. The method most commonly used is based on the assumption that beryllium-7 (^{7}Be) is a unique tracer for air parcels of stratospheric origin. Calculated correlations between surface ozone and ^{7}Be show, however, that their relationship is highly variable (e.g., Kelly et al., 1982; Ferman and Monson, 1978; Johnson and Viezee, 1981; Husain et al., 1977). Singh et al. (1980) and Viezee and Singh (1982) have pointed out problems with using this technique to quantify the contribution of stratospheric ozone to surface ozone. Singh et al. (1980) concluded that "the experimental technique involving a ^{7}Be/O_3 ratio to estimate the daily stratospheric component of ground-level O_3 is unverified and considered to be inadequate for air quality applications" (p. 1009). This group of investigators have suggested, however, that ^{7}Be may be used, under appropriate meteorological conditions, as a qualitative tracer for air masses of stratospheric origin (Johnson and Viezee, 1981; Viezee et al., 1979).

Other methods used to attempt to quantify the stratospheric component of surface ozone include aircraft observations of TF events coupled with calculations of downward ozone flux, and examination of surface ozone data records. From such data, Viezee et al. (1983) concluded that direct ground-level contributions from stratospheric ozone are infrequent (<1 percent of the time), short-lived, and associated with ozone concentrations $\leq$0.1 ppm.

Notwithstanding difficulties with quantifying its contribution to surface ozone, however, stratospheric ozone is clearly present in atmospheric surface layers, and the meteorological mechanisms responsible have been described by a number of investigators (e.g., Danielsen, 1968; Wolff et al., 1979; Johnson and Viezee, 1981).

3.7.4.7 Background Ozone from Photochemical Reactions. Whereas stratospheric ozone is thought by many investigators to be the dominant contributor to background levels of ozone, as discussed above, other investigators have concluded that as much as two-thirds of the annual average background concentrations may result from photochemical reactions. For example, Altshuller (1986), in a recent review article, has concluded that photochemically generated ozone should equal or exceed the stratospheric contribution at lower-elevation remote locations; and that photochemically generated ozone from manmade emissions probably constitutes most of the ozone measured at more polluted rural locations during the warmest months of the year. His conclusions were based, in part, on an analysis of global circulation (e.g., Levy et al., 1985) and photochemical modeling studies (e.g., Fishman and Seiler, 1983; Fishman and Carney, 1984; Fishman et al., 1985; Dignon and Hameed, 1985). In these modeling studies, the photochemical contribution to background ozone levels was estimated to range from ~15 ppb (long-term) to ~80 ppb (summertime), depending on the level of NO_x emissions assumed.

Studies on the role of NO_x in nonurban ozone photochemistry have shown that ozone formation at many of the locations is not NO_x-limited, but depends on VOC reactions as well (e.g., Martinez and Singh, 1979; Kelly et al., 1984; Liu et al., 1984). Background NO_x concentrations at most remote, clean locations range from $\lesssim$0.05 ppb upward. Mean concentrations of NO_x at nonurban locations in the United States east of the Rocky Mountains range from ~1 ppb to 10 ppb (Altshuller, 1986; see also Sections 3.5 and 3.7.5). These background concentrations of NO_x are higher than previously thought (see, e.g., Singh et al., 1980; Kelly et al., 1984, regarding global models and assumed reservoirs of NO_x).

The contributions of biogenic VOC to background ozone, although a matter of controversy in recent years, appear not to be significant under most atmospheric conditions, since ambient air concentrations of biogenic VOC are quite low, even at rural sites (Altshuller, 1983).

Thus, photochemistry and stratospheric intrusions are both regarded as contributing to background ozone concentrations, but the apportionment of background to respective sources remains a matter of investigation.

3.7.5 Sources, Emissions, and Concentrations of Precursors to Ozone and Other Photochemical Oxidants

As noted earlier, photochemical production of ozone depends both on the presence of precursors, volatile organic compounds (VOCs) and nitrogen oxides (NO_x), emitted by manmade and by natural sources; and on suitable conditions of sunlight, temperature, and other meteorological factors. Because of the intervening requirement for meteorological conditions conducive to the photochemical generation of ozone, emission inventories are not as direct predictors of ambient concentrations of secondary pollutants such as ozone and other oxidants as they are for primary pollutants.

3.7.5.1 Sources and Emissions of Precursors. Emissions of manmade VOCs (excluding several relatively unreactive compounds such as methane) in the

United States have been estimated at 19.9 Tg/yr for 1983 (U.S. Environmental Protection Agency, 1984a). Retrospective estimates show that manmade VOC emissions rose from about 18.5 Tg/yr in 1940 to about 27.1 Tg/yr in 1970 (U.S. Environmental Protection Agency, 1986). An examination of trends in manmade VOC emissions for 1970 through 1983 shows that the annual emission rate for manmade VOCs decreased some 26 percent during this period. The main sources nationwide are industrial processes, which emit a wide variety of VOCs, such as chemical solvents; and transportation, which includes the emission of VOCs in gasoline vapor as well as in gasoline combustion products. Estimates of biogenic emissions of organic compounds in the United States are highly inferential but data suggest that the yearly rate is the same order of magnitude as manmade emissions. Most of the biogenic emissions actually occur during the growing season, however, and the kinds of compounds emitted are different from those arising from manmade sources.

Emissions of manmade NO_x in the United States were estimated at 19.4 Tg/yr for 1983. Retrospective estimates show that manmade NO_x emissions rose from about 6.8 Tg/yr in 1940 to about 18.1 Tg/yr in 1970 (U.S. Environmental Protection Agency, 1986). Annual emissions of manmade NO_x were some 12 percent higher in 1983 than in 1970, but the rate leveled off in the late 1970s and exhibited a small decline from about 1980 through 1982 (U.S. Environmental Protection Agency, 1984a). The increase over the period 1970 through 1983 had two main causes: (1) increased fuel combustion in stationary sources such as power plants; and (2) increased fuel combustion in highway motor vehicles, as the result of the increase in vehicle miles driven. Total vehicle miles driven increased by 42 percent over the 14 years in question.

Estimated biogenic NO_x emissions are based on uncertain extrapolations from very limited studies, but appear to be about an order of magnitude less than manmade NO_x emissions.

3.7.5.2 Representative Concentrations in Ambient Air.

3.7.5.2.1 Hydrocarbons in urban areas. Most of the available ambient air data on the concentrations of nonmethane hydrocarbons (NMHC) in urban areas have been obtained during the 6:00 to 9:00 a.m. period. Since hydrocarbon emissions are at their peak during that period of the day, and since atmospheric dispersion is limited that early in the morning, NMHC concentrations measured then generally reflect maximum diurnal levels. Representative data for urban areas show mean NMHC concentrations between 0.4 and 0.9 ppm.

The hydrocarbon composition of urban atmospheres is dominated by species in the C_2 to C_{10} molecular-weight range. The paraffinic hydrocarbons (alkanes) are most prominent, followed by aromatics and alkenes. Based on speciation data obtained in a number of urban areas, alkanes generally constitute 50 to 60 percent of the hydrocarbon burden in ambient air, aromatics 20 to 30 percent, with alkenes and acetylene making up the remaining 5 to 15 percent (Sexton and Westberg, 1984).

3.7.5.2.2 Hydrocarbons in nonurban areas. Rural nonmethane hydrocarbon concentrations are usually one to two orders of magnitude lower than those measured in urban areas (Ferman, 1981; Sexton and Westberg, 1984). In samples from sites carefully selected to guarantee their rural character, total NMHC concentrations ranged from 0.006 to 0.150 ppm C (e.g., Cronn, 1982; Seila, 1981; Holdren et al., 1979). Concentrations of individual species seldom exceeded 0.010 ppm C. The bulk of species present in rural areas are alkanes; ethane, propane, *n*-butane, *iso*-pentane, and *n*-pentane are most abundant. Ethylene and propene are sometimes present at $\leq$0.001 ppm C, and toluene is usually present at ~0.001 ppm C. Monoterpene concentrations are usually $\leq$0.020 ppm C. During the summer months, isoprene concentrations as high as 0.150 ppm C have been measured (Ferman, 1981). The maximum concentrations of isoprene usually encountered, however, are in the range of 0.030 to 0.040 ppm C.

3.7.5.2.3 Nitrogen oxides in urban areas. Concentrations of NO_x, like hydrocarbon concentrations, tend to peak in urban areas during the early morning, when atmospheric dispersion is limited and automobile traffic is dense. Most NO_x is emitted as nitric oxide (NO), but the NO is rapidly converted to NO_2, initially by thermal oxidation and subsequently by ozone and peroxy radicals produced in atmospheric photochemical reactions. The relative concentrations of NO versus NO_2 fluctuate day-to-day, depending on diurnal and day-to-day fluctuations in ozone levels and photochemical activity.

Urban NO_x concentrations during the 6:00 to 9:00 a.m. period in 10 cities ranged from 0.05 to 0.15 ppm in studies done in the last 5 to 7 years (e.g., Westberg and Lamb, 1983; Richter, 1983; Eaton et al., 1979), although concentrations two to three times higher occur in cities such as Los Angeles. Concurrent NMHC measurements for these 10 cities showed that NMHC/NO_x ratios ranged from 5 to 16.

3.7.5.2.4 Nitrogen oxides in nonurban areas. Concentrations of NO_x in clean remote environments are usually <0.5 ppb (Logan, 1983). In exceptionally clean air, NO_x concentrations as low as 0.015 ppb have been recorded (Bollinger et al., 1982). Concentrations of NO_x at nonurban sites in the northeastern United States appear to be higher than NO_x concentrations in the west by a factor of ten (Mueller and Hidy, 1983). From the limited amount of data available, NO_x concentrations in unpopulated nonurban areas in the west average $\leq$1 ppb; but in nonurban northeastern areas average NO_x can exceed 10 ppb.

3.7.6 Source-Receptor (Oxidant-Precursor) Models

In order to apply knowledge of the atmospheric chemistry of precursors, and of ozone and other photochemical oxidants, during their dispersion and transport, models describing these phenomena have been developed in a variety of forms over the past 15 years. Most of these models relate the rates of precursor emissions from mobile and stationary sources, or precursor atmospheric concentrations, to the resulting ambient concentrations of secondary pollutants that impact receptors at downwind sites. For this reason they have been described as source-receptor models.

Current air quality, or source-receptor, models can be classified as either statistical or computational-dynamic. Statistical models are generally based on a statistical analysis of historical air quality data, and are not explicitly concerned with atmospheric chemistry or meteorology. An example of empirical models is the linear rollback concept.

Computational, or dynamic, models attempt to describe mathematically the atmospheric chemical and physical processes influencing air pollution formation and impacts. Examples of computational models include trajectory and fixed-grid airshed models. Two phenomenologically different approaches have been employed in dynamic models with respect to the coordinate systems chosen. A coordinate system fixed with respect to the earth is termed Eulerian, while in Lagrangian models the reference frame moves with the air parcel whose behavior is being simulated.

3.7.6.1 Trajectory Models. In trajectory models, a moving-coordinate system describes pollutant transport as influenced by local meteorological conditions. Trajectory models provide dynamic descriptions of atmospheric source-receptor relationships that are simpler and less expensive to derive than those obtained from fixed-cell models.

The simplest form of trajectory model is the empirical kinetic modeling approach (EKMA). This approach was developed from earlier efforts (Dimitriades, 1972) to use smog chamber data to develop graphical relationships between morning NMOC and NO_x levels and afternoon maximum concentrations of ozone. In applying EKMA, the Ozone Isopleth Plotting Package (OZIPP) (Whitten and Hogo, 1978) is used to generate ozone isopleths at various levels of sophistication corresponding to "standard" EKMA, "city-specific" EKMA, or the simplified trajectory model (F.R., 1979). The EKMA isopleths generated are used to determine the relative degree of control of precursor emissions needed to achieve a given percentage reduction in ozone.

The use of EKMA in ozone abatement programs is relatively widespread. It is therefore worth noting the general control implications of EKMA isopleths. For areas with high levels of morning precursor emissions and meteorology conducive to oxidant formation, such as Los Angeles, for example, EKMA isopleths predict that (1) at high NMOC/NO_x concentration ratios, reductions in NO_x will decrease ozone formation; (2) at moderate NMOC/NO_x ratios, reductions in NMOC and NO_x will decrease ozone formation; and (3) at very low NMOC/NO_x ratios, increases in NO_x will inhibit ozone formation. These predictions cannot be assumed to apply to all urban areas, or even to all high-oxidant urban areas, since the shape of the EKMA isopleths is a function of numerous factors, many of which are location-specific. For discussions of the specific assumptions employed in EKMA and the underlying chemistry and meteorology, the primary literature should be consulted (e.g., Dimitriades, 1970, 1972, 1977a,b; Dodge, 1977a,b; Whitten and Hogo, 1977; U.S. Environmental Protection Agency, 1977, 1978a; Whitten, 1983). Likewise, the primary literature should be consulted for additional data and discussions on the respective effects on ozone formation of controlling NMHC and NO_x (e.g., Liu and Grisinger, 1981; Chock et al., 1981; Kelly, 1985; Kelly et al., 1986; Glasson and Tuesday, 1970; Dimitriades, 1970, 1972, 1977a,b).

3.7.6.2 Fixed-Grid Models. Fixed-grid models, also called regional airshed models, are based on two- or three-dimensional arrays of grid cells and are the most sophisticated source-receptor models presently available. Such models are computationally complex and require the most extensive set of input data; but they also provide the most realistic treatment of the various processes involved in photochemical air pollution formation.

3.7.6.3 Box Models. Box models (Hanna, 1973; Demerjian and Schere, 1979; Derwent and Hov, 1980) are the simplest of dynamic models. They treat the atmosphere as a single cell, bounded by the mixing layer, having an area on the order of 100 square miles.

3.7.6.4 Validation and Sensitivity Analyses for Dynamic Models. All presently available source-receptor models require a degree of simplifying assumptions to deal with practical limitations imposed by existing computer capabilities, time and cost constraints, or lack of knowledge concerning inputs such as boundary conditions, emissions, or detailed reaction mechanisms. The reliability and applicability of any particular model therefore depends upon its specific limitations, data requirements, and degree of validation against experimental data from ambient air measurements or environmental chamber runs. Reliability and applicability also depend on the quality of the chemical kinetics mechanisms used to define the O_3-HC-NO_x relationship.

Attempts are made to validate model predictions by comparing them with real observations; and operating parameters are often varied to determine the sensitivity of the model to respective parameter changes (Gelinas and Vajk, 1979). In addition, the extent of agreement between the results from two simulations can be tested. In this way, completely different models may be compared, or an internal component, such as the chemical kinetics mechanisms, may be substituted and the model run again to ascertain the effect of such substitutions.

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4. SAMPLING AND MEASUREMENT OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS AND THEIR PRECURSORS

4.1 INTRODUCTION

Detailed information is presented in this chapter on methods for sampling and measuring ozone, "total oxidants," hydrogen peroxide, and peroxyacetyl nitrate and its higher homologues. Because of their utility in atmospheric research and in the application of oxidant abatement programs, methods for sampling and measuring the organic and inorganic precursors to oxidants are described as well. The information presented here should prove helpful to state and local air pollution agencies and to researchers investigating health and welfare effects. The chief reason for presenting such information, however, is to provide relevant information: (1) for assessing the accuracy of aerometric data on these pollutants; and (2) for determining the impact of respective measurement and calibration methods on existing data on the health and welfare effects of ozone, total oxidants, and individual other oxidants. Primary emphasis is placed in this chapter on techniques considered satisfactory for routine monitoring, on the effects of changes in calibration procedures for ozone measurements, on the relationship between ozone and "total oxidant" measurements, and on the accuracy and reliability of methods for measuring oxidants not routinely monitored in ambient air.

Since the publication of the 1978 criteria document on ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978a), a new procedure for calibrating ozone measurements has been promulgated by EPA as the Federal Reference Method for calibration. In addition, EPA has continued efforts to institute and codify a formal nationwide program of quality assurance for the routine monitoring of pollutants in ambient air. Some examples of these procedures are documented in this chapter as they apply to actual operation of the analytical instrumentation. Detailed descriptions of analytical procedures, quality assurance procedures, and reporting requirements are contained in Quality Assurance Handbook for Air Pollution Measurement Systems (U.S. Environmental Protection Agency, 1977b). Pertinent rules and regulations are contained in the Federal Register (1979a,b,c,d,e).

Brief summaries are provided below of requirements pertaining to quality assurance and sampling for ozone monitoring.

4.2 QUALITY ASSURANCE AND OTHER SAMPLING FACTORS IN MONITORING FOR OZONE

4.2.1 Quality Assurance in Ambient Air Monitoring for Ozone

Quality assurance as defined by EPA rules and regulations consists of two distinct functions. One is the assessment of the quality of monitoring data by estimating their precision and accuracy. The other is the control and possible improvement of the quality of the ambient air data by implementation of quality control policies, procedures, and corrective actions.

Each quality control program, developed by the individual States and approved by the EPA Regional Administrator, must include operational procedures for each of the following activities:

1. Selection of methods, analyzers, or samplers (prescribed reference and equivalent methods for ambient air monitoring are described elsewhere in this chapter);
2. Installation of equipment;
3. Calibration (test concentrations for ozone must be obtained by means of the ultraviolet (UV) photometric calibration procedure described elsewhere in this chapter or by means of a certified ozone transfer standard);
4. Zero/span checks and adjustments of automated analyzers;
5. Control checks and their frequency;
6. Control limits for zero, span, and other control checks, and respective corrective actions when such limits are surpassed;
7. Calibration and zero/span checks for multiple range analyzers;
8. Preventive and remedial maintenance;
9. Quality control procedures for air pollution episode monitoring;
10. Recording and validation of data;
11. Documentation of quality control information.

A one-point precision check must be carried out at least every 2 weeks on each automated analyzer used for ozone, using a precision test gas of known concentration. Each calendar quarter, at least 25 percent of the analyzers used by the State and Local Air Monitoring Stations (SLAMS) for monitoring ozone must be formally audited by an independent operator by challenging with at least one audit gas of known concentration in each of the four concentration ranges. Similar requirements are set forth for monitoring networks designed to assess Prevention of Significant Deterioration (PSD) requirements.

In addition to requirements and recommendations associated with the selection, installation, and maintenance of monitoring equipment, the above-cited Federal Register publications discuss certain design criteria for monitoring networks (SLAMS and the National Aerometric Monitoring Stations, NAMS). Included are requirements on siting of monitors in order to obtain ozone concentrations that are representative of regions of varying dimensions. For example, a "middle scale" monitor would represent conditions close to sources of NO_x such that local ozone scavenging effects might be of significance. A "neighborhood scale" monitor, on the other hand, would be located somewhere in a reasonably homogeneous urban subregion having dimensions of a few kilometers. Other "scales" applicable to siting of ozone monitors include urban scale, which would be used to estimate concentrations characteristic of an area having dimensions between several and 50 kilometers or to measure high concentrations downwind of an area with high precursor emissions; and regional scale, used to typify concentrations over portions of a major metropolitan complex up to dimensions of hundreds of kilometers. For ozone SLAMS stations, applicable scales are middle, neighborhood, urban, and regional. Requirements for NAMS stations for ozone are neighborhood and urban scale. Two ozone NAMS stations are expected to be sufficient for each urban area: one for specific transport conditions leading to high ozone; and the other for monitoring peak concentrations relative to population exposure.

4.2.2 Sampling Factors in Ambient Air Monitoring for Ozone

Sampling factors may have a crucial effect on the quality and utility of measurements both in ambient air and in controlled laboratory situations. Sampling techniques and strategies must preserve the integrity of a representative fraction of ambient air and must be consistent with the specific purpose of the measurement. In this section, the significance of some sampling factors will be discussed briefly. For more detailed discussions of this subject, the reader is referred to Ott (1977) and to reports prepared for EPA by the National Research Council (U.S. Environmental Protection Agency, 1977a; National Research Council, 1977).

4.2.2.1 Sampling Strategies and Air Monitoring Needs. Air monitoring data relevant to assessing ambient O_3 or oxidant levels are collected for a variety of specific needs, including:

1. Data to be used in trend analysis as indicators of the state of attainment of ambient air quality standards.
2. Data to be used in development of O_3 control strategies and evaluation of their effectiveness.
3. Data to be used in the development and validation of air quality simulation models capable of application to the O_3 problem.
4. Data to be used in investigation of causes of the ozone problem both in general and in specific localities.
5. Data to be used in special research studies such as the effects of ambient air pollution on human health and welfare.

Each specific purpose or need requires special considerations with regard to air sampling strategy. For example, 5 or more years of O_3 data might be required for the adequate assessment of trends that resulted from the application of a particular control strategy rather than trends that resulted from chance local meteorological conditions. In contrast, the validation of an air quality simulation model might require only a few carefully chosen days of very detailed measurements of O_3, hydrocarbons, and NO_x, as well as detailed meteorological data and time-varying emissions along the trajectory of the air parcel in question.

4.2.2.2 Air Monitoring Site Selection. Ozone in the lower troposphere is a product of photochemical reactions that involve sunlight, hydrocarbons, and oxides of nitrogen. In typical urban atmospheres, ozone precursors react to produce ozone at such a rate that the O_3 reaches its daily peak level in the middle of the day at locations downwind from the source-intensive center-city area. Thus, if peak O_3 concentrations are to be measured, monitoring stations should, in general, be located downwind from city centers. This downwind distance may be on the order of 15 to 30 kilometers (9 to 19 miles), depending on predominant wind patterns in the area (U.S. Environmental Protection Agency, 1977a). This distance may be highly area-specific, however. For example, ozone maxima in the Los Angeles plume have been observed as far downwind as 50 to 70 km.

Once a station is located, additional sampling considerations arise because of the chemical reactivity and instability of the O_3 molecule. Ozone reacts extremely rapidly with NO and with some hydrocarbon compounds, including most of those emitted by vegetation. Also, O_3 decomposes readily on contact with the surface of many materials. Consideration of these effects led to the development of specific criteria for locating an O_3 monitoring station (U.S. Environmental Protection Agency, 1977a; National Research Council, 1977). Briefly, the inlet of the sampling probe of the ozone analyzer should be positioned 3 to 15 meters (10 to 49 feet) above ground, at least 4 meters (13 feet) from large trees, and 120 meters (349 feet) from heavy automobile traffic. Sampling probes should be designed so as to minimize O_3 destruction by surface reaction or by reaction with NO.

Another consideration that has significance for the selection of sites for air monitoring stations is the fact that ambient monitoring data, as routinely obtained, have limited validity as absolute measures of air quality. This limitation arises from the fact that, at ground level, the ambient atmosphere is inhomogeneous as a result of a continuous influx of fresh emissions, incomplete mixing, and destruction of O_3 by fresh and unreacted emissions and destruction on surfaces. In view of such inhomogeneity, monitoring data from a fixed network provide measures of air quality at a discrete number of locations but may not detect temporal and spatial variations in ozone concentrations of a localized nature. This problem can be alleviated by use of a greater density of monitoring stations or by use of a validated air quality model. Such models are capable of helping quantify the emission, dispersion, and chemical reaction processes. Their outputs can provide data on the distribution of air quality concentrations between widely spaced ambient monitors.

The emphasis in this section has been on a brief discussion of sampling strategies. The word sampling is also widely considered to mean those techniques that are required to obtain a parcel of air that is representative of the polluted atmosphere, and to maintain its integrity until a measurement of concentration has been carried out. Considerations relating to this meaning of sampling are discussed as appropriate in the following sections on measurement techniques.

4.2.3 Measurement Methods for Total Oxidants and Ozone

4.2.3.1 Total Oxidants. Although ozone was first unambiguously identified in polluted atmospheres by infrared spectroscopy (Stephens et al., 1956b; Scott et al., 1957), the earliest procedures for routinely monitoring O_3 and other oxidizing species in the atmosphere were based on iodometry. Iodometric techniques are inherently non-specific in that a variety of oxidizing species in addition to O_3 may be positive interferences, whereas reducing agents are negative interferences. Thus, the name "total oxidants" was coined because the technique responded to O_3 and other oxidants such as peroxides, peroxyacetyl nitrate (PAN), and nitrogen dioxide (NO_2). Total oxidants are then actually defined by the particular iodometric procedure used, since the response to the various oxidizing species present will depend on the details of the procedure. This will be more evident when interferences are discussed below. The use of the word "total" is in itself a misnomer. The measurement does not reflect a sum of the oxidizing species present because the various oxidants present in the atmosphere react to produce iodine at different stoichiometries and different rates. In spite of these difficulties, the measurement of total oxidants was a useful method for characterization of the atmosphere because of its correlation with the principal oxidant, O_3; and, consequently, there is a large oxidant data base available. For these reasons, the two principal methods used for monitoring total oxidants are discussed briefly below.

The bulk of the total oxidants data base was obtained by the use of two types of continuous monitoring instruments. In both types, an air sample is continuously scrubbed by an aqueous reagent containing potassium iodide (KI). Ozone and other oxidants produce iodine (tri-iodide ion) according to the reaction:

$$O_3 + 3I^- + H_2O \rightarrow I_3^- + O_2 + 2OH \qquad (4\text{-}1)$$

In colorimetric oxidant instruments, the iodine is measured photometrically by ultraviolet absorption (Littman and Benoliel, 1953). In the other common type analyzer the iodine produced is measured by electrochemical means (Brewer and Milford, 1960; Mast and Saunders, 1962). Many other chemical techniques for oxidants have been proposed and in some cases applied, but for these reference is made to the original literature (Hodgeson, 1972; Katz, 1976).

The interferences for both colorimetric and amperometric O_3 analyzers are other oxidizing and reducing species in the atmosphere. The major oxidant in ambient air by far is O_3 (Chapter 5); and the other oxidants present, except NO_2, are considered part of the total oxidants measured rather than interferences. The only significant reducing interference known is SO_2.

The magnitude of the NO_2 interference is variable (Tokiwa et al., 1972; Intersociety Committee, 1970). For the Brewer amperometric cell, the interference from NO_2 is only 6 percent of an equivalent concentration of O_3 (Tokiwa et al., 1972). For colorimetric oxidant analyzers, NO_2 interference equivalents vary from 20 to 32 percent depending on O_3 concentration (Tokiwa et al., 1972). A "corrected" oxidant measurement is obtained by simultaneous measurement of NO_2 and correction of the corresponding total oxidant measurement. The interference from SO_2 is quantitative for both colorimetric and electrochemical oxidant measurements, with one mole of SO_2 consuming one mole of tri-iodide ion. If the SO_2 concentration is less than that of total oxidant and SO_2 is simultaneously measured, the total oxidant may also be corrected for SO_2. This was the procedure previously applied in the older aerometric data for California. For many areas of the East Coast and Midwest, such a correction was not possible and preferential SO_2 scrubbers were used (Saltzman and Wartburg, 1965; Mueller et al., 1973). These scrubbers could be effective in the hands of skilled operators but their use was not without problems. Among these problems were partial oxidation of NO to NO_2 and of H_2S to SO_2, and partial removal of O_3 when the scrubber was wet or contaminated (Hodgeson, 1972).

4.2.3.2 Ozone

4.2.3.2.1 Gas-phase chemiluminescence. Many of the O_3 oxidation reactions are sufficiently energetic that they produce electronically excited products, intermediates, or reactants, which in turn may chemiluminesce (Zocher and Kautsky, 1923; Bowman and Alexander, 1966). Although well known for many years, such reactions were not applied to chemical analysis until the 1960s. In 1965, Nederbragt reported a detector that employed chemiluminescence from the reaction of O_3 with ethylene for measurement of O_3 in the vicinity of large accelerators (Nederbragt et al., 1965; Warren and Babcock, 1970). Applications to atmospheric analysis were a natural consequence (Stevens and Hodgeson, 1973). The reference method for O_3 originally promulgated by EPA for compliance monitoring was the O_3-ethylene chemiluminescence method (F.R., 1971). Appendix D of 40 CFR, Part 50, describes the principle of the method, including a method of calibration (F.R., 1971; C.F.R., 1971). Since then, the measurement principle has remained the same but calibration procedures have undergone extensive revision as discussed below (Section 4.2.4). It is also noteworthy that the reference method is specific for O_3, whereas the data used for establishing the standard were based on measurement of total oxidants. This issue is addressed in Section 4.2.5.

A flow of sample air (1 to 5 liter/min) containing O_3 and a small flow of pure ethylene are mixed at atmospheric pressure in a small reaction chamber closely coupled to the photocathode of a photomultiplier tube. The reaction between O_3 and ethylene produces a small fraction of electronically excited formaldehyde. Chemiluminescence from this excited state results in a broad emission band centered at 430 nm (Finlayson et al., 1974). The emission intensity that is monitored is a linear function of O_3 concentration from 0.001 to greater than 1 ppm. The relation between intensity and concentration, i.e., instrument calibration, must be determined for each instrument with standard concentrations of O_3 in air. The minimum detection limit and the response time are functions of detector design. Detection limits of 0.005 ppm and response times of less than 30 seconds are readily attained, however, with modest design features. For example, cooling the photomultiplier improves the sensitivity but is not normally required. There are no known interferences among the common atmospheric pollutants. There have been reports of a positive interference when O_3 is measured in the presence of water vapor, i.e., a signal enhancement of 3 to 12 percent in high humidity as opposed to measurement of the same concentration of O_3 in dry air (California Air Resources Board, 1976). Where this may be a real problem, it can be minimized by performing calibrations with humidified air. Finally, in order to obtain acceptable measurement precision and constant span, analyzers must contain means for maintaining constant air and ethylene flow rates.

Ambient air monitoring reference and equivalent methods have been published by EPA (F.R., 1975a). This regulation prescribes methods of testing and performance specifications that commercial analyzers must meet in order to be designated as a reference method or as an equivalent method. An analyzer may be designated as a reference method if it is based on the same principle as the reference chemiluminescence method and meets performance specifications. An automated equivalent method must meet the prescribed performance specifications and show a consistent relationship with a reference method. These specifications for O_3 analyzers are listed in Table 4-1. Commercial analyzers that have been designated as reference or equivalent methods are listed in Table 4-2. Information concerning the applications supporting the designation of analyzers as reference or equivalent methods may be obtained by writing the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

4.2.3.2.2 Gas-solid chemiluminescence. The first chemiluminescence technique for O_3 was developed by Regener for stratospheric measurements (Regener, 1960) and later for measurements in the troposphere (Regener, 1964). The reaction of O_3 with Rhodamine-B adsorbed on activated silica gel produces chemiluminescence in the red region of the spectrum characteristic of the fluorescence spectrum of Rhodamine-B. The intensity is a linear function of O_3 concentration, the minimum detection limit can be lower than 0.001 ppm, and no atmospheric

TABLE 4-1. PERFORMANCE SPECIFICATIONS FOR AUTOMATED METHODS OF OZONE ANALYSIS

Performance parameter	Units	Specification
Range	ppm	0 to 0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interference	ppm	±0.02
Total interference	ppm	0.06
Zero drift, 12 and 24 hour	ppm	±0.02
Span drift, 24 hour		
20% of upper range limit	percent	±20.0
80% of upper range limit	percent	±5.0
Lag time	minutes	20
Rise time	minutes	15
Fall time	minutes	15
Precision		
20% of upper range limit	ppm	0.01
80% of upper range limit	ppm	0.01

Source: F.R. (1975a); C.F.R. (1975).

TABLE 4-2. LIST OF DESIGNATED REFERENCE AND EQUIVALENT METHODS OF OZONE ANALYSIS

Identification and source	Fed. Register notice			Ref.	Designation (E=equiv. R=ref.)
	Vol.	Page	Date		
Beckman Model 950A Ozone Analyzer Beckman Instruments 2500 Harbor Boulevard Fullerton, CA 92634	42	28571	6/03/77	(F.R., 1977a)	R
Bendix Model 8002 Ozone Analyzer The Bendix Corporation Post Office Drawer 831 Lewisburg, WV 24901	41 45	5145 18474	2/04/76 3/21/80	(F.R., 1976a) (F.R., 1980a)	R
Columbia Scientific Industries Model 2000 Ozone Meter 11950 Jollyville Road Austin, TX 78759	44	10429	2/20/79	(F.R.,1979a)	R
Dasibi Model 1008-AH Ozone Analyzer	48	10126	3/10/83	(F.R., 1983)	E
Dasibi Model 1003-AH 1003-PC or 1003-RS Ozone Analyzers Dasibi Environmental Corp. 616 E. Colorado Street Glendale, CA 91205	42	28571	6/03/77	(F.R., 1977a)	E
MEC Model 1100-1 Ozone Meter, MEC Model 1100-2 Ozone Meter, or MEC Model 1100-3 Ozone Meter Columbia Scientific Industries 11950 Jollyville Road P.O. Box 9908 Austin, TX 78766	41 42	46647 30235	10/22/76 6/13/77	(F.R., 1976b) (F.R., 1977b)	R
Meloy Model OA 325-2R Ozone Analyzer	40	54856	11/26/75	(F.R., 1975b)	R
Meloy Model OA 350-2R Ozone Analyzer Columbia Scientific Industries 11950 Jollyville Road Austin, TX 78759	40	54856	11/26/75	(F.R., 1975b)	R

TABLE 4-2 (continued). LIST OF DESIGNATED REFERENCE AND EQUIVALENT METHODS OF OZONE ANALYSIS

Identification and source	Fed. Register notice Vol.	Page	Date	Ref.	Designation (E=equiv. R=ref.)
Monitor Labs Model 8810 Photometric Ozone Analyzer Monitor Labs, Incorporated 10180 Scripps Ranch Boulevard San Diego, CA 92131	46	52224	10/26/81	(F.R., 1981)	E
Monitor Labs Model 8410E Ozone Analyzer Monitor Labs, Incorporated 10180 Scripps Ranch San Diego, CA 92121	41	53684	12/08/76	(F.R., 1976d)	R
PCI Ozone Corporation Model LC-12 Ozone Analyzer PCI Ozone Corporation One Fairfield Crescent West Caldwell, NJ 07006	47	13572	03/31/82	(F.R., 1982)	E
Philips PW9771 O_3 Analyzer Philips Electronic Instruments, Incorporated 85 McKee Drive Mahwah, NJ 07430	42 42	38931 57156	08/01/77 11/01/77	(F.R., 1977c) (F.R., 1977d)	E
Thermo Electron Model 49 UV Photometric Ambient O_3 Analyzer Thermo Electron Corporation Environmental Instruments Division 108 South Street Hopkinton, MA 01748	45	57168	08/27/80	(F.R., 1980b)	E

interferences have been observed (Hodgeson et al., 1970). The technique is, in fact, more sensitive than the gas-phase Nederbragt method and does not require critical control of flow rate. It had the disadvantage in the original analyzer built, however, that frequent and periodic internal calibration cycles were required to compensate for changes and decaying sensitivity of the surface of the detector (Regener, 1964; Hodgeson et al., 1970).

Improvement was made in the stability of the surface response in a modification added by Bersis and Vassiliou (1966), in which gallic acid is also adsorbed on the surface in excess. The O_3 apparently reacts with and consumes the gallic acid rather than Rhodamine-B. An energy transfer step to Rhodamine-B subsequent to the initial reaction results in the same chemiluminescence from the dye compound, which is now no longer consumed. A commercial analyzer, Phillips Model PW9771, is based on this principle and has been designated as an equivalent method under EPA regulations.

4.2.3.2.3 Ultraviolet photometry. Ozone has a moderately strong absorption band in the ultraviolet (UV), with a maximum very near the mercury 254 nm emission line. This band is essentially a continuum near 250 nm. The molar absorption coefficient at the mercury line has been measured by several investigators with good agreement and has an accepted value of 134 ± 2 M^{-1} cm^{-1} (base 10) at 0°C and 1 atm (Hampson et al., 1973). Ultraviolet absorption has long been used as a method of measuring gas-phase O_3 in fundamental chemical and physical studies. Some of the first atmospheric O_3 measurements were, in fact, made by UV photometry; e.g., the Kruger Photometer. These early instruments and the problems with their use are described more completely in the first criteria document for photochemical oxidants (National Air Pollution Control Administration, 1970). The major problem with the older photometric instruments was the large imprecision involved in measuring the very small absorbance values obtained.

This problem of adequate sensitivity with moderate pathlengths has been overcome by modern digital techniques for measuring small absorbancies. The first instrument of this new generation of photometers was marketed by Dasibi of Glendale, California, in the early 1970s. The details of this instrument have been described by Bowman and Horak (1972). Other commercial instruments have since been marketed and, along with the Dasibi, have been designated as equivalent methods by EPA (Table 4-2). All of these instruments operate effectively as double-beam digital photometers. A transmission signal is averaged over a finite period of time with O_3 present and is compared to a similar transmission signal obtained through an otherwise identical reference air stream from which the O_3 has been preferentially scrubbed; e.g., using a manganese dioxide scrubber. The electronic comparison of the two signals can be converted directly into a digital display of O_3 concentration.

The UV photometric technique has the advantages, like gas-solid chemiluminescence, that a reagent gas flow is not required and that sample air flow control is not critical. In addition, the measurement is in principle an absolute one, in that the concentration can be computed directly from the measured absorbance since the absorption coefficient and the pathlength are known. This capability is used extensively for the purpose of O_3 calibration as discussed in Section 5.5.5. Commercial UV photometers for O_3 can serve a dual function as a standard for O_3 calibration and as a means for measuring ambient ozone concentrations. In practice, UV photometric analyzers that are used for monitoring O_3 concentrations in the atmosphere are calibrated with standard O_3 samples in order to compensate for possible O_3 losses in the sampling and inlet systems. A UV photometric analyzer has the potential disadvantage that any molecular species that absorbs at 254 nm (e.g., SO_2, benzene, mercury vapor) and that may also be removed along with O_3 during the reference cycle can interfere. Documentation of such interference during atmospheric monitoring is lacking at present.

4.2.4 Generation and Calibration Methods for Ozone

Unlike the other criteria pollutants, O_3 is a thermally unstable species that must be generated in situ during the calibration of analyzers used for atmospheric monitoring. This creates special requirements not encountered with other pollutants and thus this section deals with means for generating dynamic air streams containing stable O_3 concentrations and chemical and physical means for absolute measurement of these concentrations.

4.2.4.1 Generation. Ozonized samples of air can be produced by a number of means, including photolysis (Brewer and Milford, 1960), electrical discharge (Toyama and Kobayashi, 1966), and radiochemical methods (Steinberg and Dietz, 1969). Electrical discharges are useful for producing high concentrations of O_3 in air for other applications; e.g., O_3 chemistry. Radiochemical methods would be ideal except for their cost and required safety features. By far the most common method, however, for generating low concentrations of O_3 in air involves the photolysis of molecular oxygen.

$$O_2 + h\gamma(\lambda<200\ \text{nm}) \rightarrow 2O \qquad (4\text{-}2)$$

$$O + O_2 + M\ (M = N_2 \text{ or } O_2) \rightarrow O_3 + M \qquad (4\text{-}3)$$

One of the most common photolytic generators uses a mercury vapor 6- or 8-inch PenRay photolysis lamp positioned parallel to a quartz tube through which air flows at a controlled rate. The O_3 concentration is simply varied by means of an adjustable and calibrated mechanical sleeve placed over the lamp envelope (Hodgeson et al., 1972) or by varying the voltage or current supplied to the lamp.

4.2.4.2 Calibration

4.2.4.2.1 KI procedures: original EPA reference method. The output of photolytic O_3 generators can provide air samples containing stable O_3 concentrations over a considerable period of time with careful control of flow rate, lamp voltage, temperature, and pressure. It is necessary to calibrate these generators periodically with an absolute reference method. Prior to 1975, there were as many as seven different calibration methods for O_3 employed to varying extents in this country (National Research Council, 1977). In an attempt to standardize the methodology, EPA published a reference calibration procedure with the reference method in 1971 when the oxidant (as O_3) standards were promulgated (F.R., 1971). This method was the 1 percent neutral buffered potassium iodide (NBKI) procedure, a technique that had been used by EPA and other agencies for some time.

During the early 1970s, it became evident that there were serious deficiencies with the NBKI reference method. Several problems with the NBKI procedure, summarized by a joint EPA-NBS workshop in 1974 (Clements, 1975), included the gradual continued release of iodine after sampling, variable results obtained with different types of impingers, reagent impurities, and a positive bias when compared to other O_3 measurement methods. An interagency collaborative study was undertaken to intercompare iodometric methods used by the Los Angeles Air Pollution Control District (LAAPCD), the California Air Resources Board (CARB), and EPA, using UV photometric O_3 measurements as the reference. The results of this study (DeMore et al., 1976) demonstrated the positive bias of the NBKI methods. Concurrent with and after these earlier reports, a large number of individual studies ensued. The history of these studies has been reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1978a) and by Burton et al. (1976). The major conclusions from these studies are presented below.

1. Results obtained by NBKI procedures are higher than those obtained by UV photometry or gas-phase titration by 5 to 25 percent, depending on details of the procedure.

2. When O_3 is measured in the presence of humidified air, NBKI results tend to be even higher by another 5 to 10 percent (e.g., California Air Resources Board, 1976). The reason for this apparent moisture effect is not known.
3. In general, NBKI techniques are subject to large imprecision because of procedural variation.

The EPA then evaluated four alternative calibration procedures (Rehme et al., 1981) and selected UV photometry as the reference procedure because of its superior accuracy and precision and its simplicity of use.

Although NBKI methods are no longer used in this country for the purpose of calibration, there is a considerable data base available on health and welfare effects, as well as atmospheric chemistry and monitoring, that is based on these methods as standards. Therefore, it is important to consider how these data may be evaluated and compared to newer effects and aerometric data based on the new UV calibration standard. Since a systematic bias is known to exist between calibrations by KI methods and UV photometric methods, it should be possible, in principle, to apply correction factors to convert from a KI reference to a UV photometric reference. There are several problems inherent in attempting such corrections, however. A fairly wide range of variations has been reported in the literature on the comparison of KI and UV photometric measurements. As discussed previously, the presence of moisture in the calibration air increases the magnitude of the bias. Fortunately, both the CARB and the LAAPCD procedures called for the consistent use of humidified air, whereas the EPA reference method prescribed the use of dry air. In addition, the elapsed time between sample collection and color measurement will also affect the magnitude of the bias because of the slow liberation of iodine after sampling (Clements, 1975; Beard et al., 1977; Hodgeson, 1976). Other unknown experimental factors may also influence the bias, e.g., impinger design (Clements, 1975; Beard et al., 1977).

An assessment has been made of the previous KI versus UV intercomparisons, and recommendations are given in Table 4-3 for correction factors to apply to calibration data for conversion from UV to a KI reference or vice versa. It should be emphasized that these factors could validly be applied to correct for a calibration bias only and can not be applied for comparison of data where other effects are present, e.g., the comparison of oxidants versus O_3

TABLE 4-3. FACTORS FOR INTERCOMPARISON OF DATA CALIBRATED BY UV PHOTOMETRY VERSUS KI COLORIMETRY

Calibration method	Ratio, KI/UV
EPA, 1% NBKI	1.12 ± 0.05
CARB, 2% NBKI	1.20 ± 0.05
LAAPCD, 1% UKI	0.96[a]

[a] Correction for this method not recommended; only one intercomparison has been reported.

data where the effects of oxidizing or reducing interferences must be considered. In this assessment, consideration was given only to those studies in which the KI procedure was compared directly to UV photometry. The recommended value for data based on the CARB method assumes the use of humidified air. The value recommended for the EPA method assumes that dry air was used and that color measurement was made immediately after sample collection.

The uncertainties assigned reflect the fact that a range of values has been reported for the ratios in previous studies. Finally, whenever any attempt is made to convert from one data base to another, these uncertainties must be added by conventional error propagation techniques to the uncertainty inherent with the original measurement.

4.2.4.2.2 Ultraviolet photometry method. A major reason UV photometry was designated as the calibration procedure was the excellent precision of the photometric measurement. In the collaborative study by Rehme et al. (1981), measurement with ten individual UV photometers gave only a 3.4 percent variability when compared to a reference measurement system. Other significant factors in the selection of UV photometry were the inherent simplicity of UV photometric measurements and the ready availability of commercial instruments that can also serve well as transfer standards between laboratory photometers and field O_3 analyzers. (See National Research Council, 1977, and McElroy, 1979, for a discussion of transfer standards.)

It was also presumed that UV photometry gives more accurate results, since the accuracy is determined primarily by the O_3 absorption coefficient, which is well known (Hampson et al., 1973; DeMore and Patapoff, 1976). Although there is little doubt that the accuracy of O_3 measurements has been significantly improved by conversion to the UV basis, some question still exists regarding the absolute relation between O_3 measurements by UV photometry and O_3 measurements by GPT measurements based on either an NBS standard reference material (SRM) nitric oxide (NO) gas cylinder or an NO_2 SRM permeation tube. These intercomparisons have been made by several investigators over the past 10 years and have been summarized by Burton et al. (1976) and Paur and McElroy (1979). The agreement between GPT and UV measurements was generally close to unity, although in some cases O_3 measurements by GPT have shown a small positive bias with respect to UV measurements (e.g., Rehme et al., 1981; DeMore et al., 1976). DeMore and Patapoff (1976) reported a ratio of unity between simultaneous measurements of O_3 by GPT and UV with a 5 percent uncertainty on the ratio of these measurements. In a recent detailed study conducted at the National Bureau of Standards (NBS) (Fried and Hodgeson, 1982), O_3 measurements made with an NBS standard photometer (Bass et al., 1977) were compared to GPT measurements of O_3 that were standardized against both NO cylinders (NBS SRM) and NO_2 permeation tubes (NBS SRM). Since the measurement of flow rates is a critical GPT variable and has been considered as a major source of error in GPT measurements (DeMore and Patapoff, 1976), NBS facilities were used for making absolute flow measurements by both gravimetric and volumetric means. The results of this study were that values of O_3 measured by GPT based on NO_2 or NO SRMs agreed to within less than 1 percent, but that values of O_3 measured by UV were lower by 3 percent. For a consideration of possible error sources, reference is made to the original article (Fried and Hodgeson, 1982). In summary, the UV photometric O_3 standard agrees quite closely with the NO and NO_2 measurement standards by GPT, as it should in principle. The resolution of any small biases that remain seems an appropriate matter for consideration by EPA and NBS.

The measurement principle for the absolute measurement of O_3 by UV photometry is the same as that used by instruments for monitoring atmospheric O_3 as described in Section 4.2.3.2.3 (Bowman and Horak, 1972; DeMore et al., 1976; Bass et al., 1977). Ozone is measured in a dynamic flow system by measuring the transmission, I/Io, of ozonized clean air in an absorption cell of pathlength ℓ. When the concentration is to be expressed in units of ppm, measurement of temperature and pressure is also required. The O_3 concentration may then be calculated directly from the Beer-Lambert equation:

$$[O_3]_{ppm} = \frac{10^6}{\alpha \ell} \times \frac{T}{273} \times \frac{760}{P} \ln \frac{Io}{I} \qquad (4\text{-}4)$$

where α = O_3 absorption coefficient at 254 nm, 1 atm, and 0°C,
= 308 ± 4 $atm^{-1}cm^{-1}$ (log base e),

and

T = temperature, °K;
P = pressure, torr.

Laboratory photometers used for primary O_3 calibrations have pathlengths of 1 to 5 meters and sophisticated digital electronic means for measuring small absorbancies (Bass et al., 1977; Bowman and Horak, 1972).

The conversion of a commercial O_3 photometric monitor to a photometer for use as a transfer standard for calibration has been described by Paur and McElroy (1979). Definitions are in order here. A primary standard UV photometer is one that meets the requirements and specifications given in the 1979 revision of the O_3 measurement and calibration procedures (F.R., 1979e). A transfer standard as used by EPA is a device or a method that can be calibrated against a primary photometer and transferred to another location for calibration of O_3 analyzers. Commercial O_3 photometers have served well in this regard, but other devices have been used as well; e.g., calibrated generators and GPT apparatus. Guidelines on transfer standards for O_3 have been published by EPA (McElroy, 1979), and reference has already been made to the NAS discussion on transfer standards (National Research Council, 1977).

The use of UV photometry is unique in air pollution measurements in that it is based on a physical measurement principle rather than a chemical standard. It is then worthwhile to trace how the measurement chain works from a primary standard to field measurements. The primary standard is referenced to the accepted O_3 absorption coefficient. Transfer standards are then calibrated with primary photometers maintained at EPA, NBS, and elsewhere. The use of commercial photometers in this regard has been described by several investigators (DeMore et al., 1976; Hodgeson et al., 1977). These and other kinds of transfer standards are then used to calibrate O_3 analyzers used for field measurements.

4.2.4.2.3 Other procedures. Although UV photometry has been specified as the reference calibration procedure, other procedures are available that can give equivalent results. These include a modified KI method, which was allowed as an interim alternative method for the calibration of O_3 monitors when the UV method was designated in 1979. Other KI methods that have been used successfully in Europe are also briefly discussed here. Finally, the GPT method is reviewed since it has been used extensively in this country and was discussed above with regard to the cross-check of method accuracies.

A major problem with NBKI techniques is the slow release of iodine and continued color development after sampling. Flamm (1977) evaluated the rate of this iodine production and found that it was the same as the rate with which hydrogen peroxide (H_2O_2) releases iodine from the same solution. Based on this observation and a consideration of other possible species that might be responsible, Flamm concluded that certain buffer anions, including phosphate, catalyze the formation of H_2O_2 and yield stoichiometries for iodine production greater than 1. Measurements made with a 1 percent KI reagent containing 0.1 M boric acid (BAKI), pH=5, did not exhibit this phenomenon, nor did the original EPA method when phosphate was omitted from the reagent (Hodgeson, 1976).

The BAKI method was evaluated as one of four alternative techniques in the collaborative study conducted by EPA (Rehme et al., 1981). No significant bias was observed between BAKI and the reference technique based on UV photometry. An analysis, however, of BAKI measurements by ten volunteers revealed a large system-dependent variability, and thus the BAKI technique was not recommended as an independent calibration method. It is noteworthy that the system variability attributable to calibration was reduced somewhat if each operator assumed a molar absorption coefficient for iodine (as I_2) of $2.56 \times 10^4\ M^{-1}cm^{-1}$ at 352 nm rather than independently measuring the absorption coefficient with standard I_2 solutions as these procedures usually prescribe. Measurement systems based on the BAKI procedure may still be certified as transfer standards provided the guidelines for certification given in the EPA technical assistance document for such standards are followed (McElroy, 1979).

Methods based on iodometry have been used in Europe for some time for the calibration of O_3 analyzers. Bergshoeff (1970) described a method for use in the Netherlands, in which thiosulfate is added to the KI reagent (KIT method) along with 0.1 M phosphate buffer. The iodine released is immediately reduced by the thiosulfate and the amount of iodine consumed is determined by back-titration of the thiosulfate. This method has the advantage that problems associated with iodine instability in solution are eliminated. In the Federal Republic of Germany, the standard is based on a 2 percent KI reagent with 2 percent KBr (KIBr Method) and a low concentration (0.02 to 0.03 M) of phosphate buffer (Van de Wiel et al., 1979). These techniques have been compared to UV and GPT measurement procedures by Van de Wiel et al. (1979). Measurements made with the KIBr method were in essential agreement with measurements by UV or GPT, while measurements by the KIT method were too high by 15 to 25 percent, depending on the relative humidity of the samples. Modifications have since been made in the KIT method by the addition of KBr and reduction of the phosphate concentration.

The gas-phase titration (GPT) method employs the moderately rapid bimolecular reaction between O_3 and NO to produce NO_2 (Rehme et al., 1974):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4\text{-}5)$$

This approach was, in fact, one of the early methods used to measure the absorption coefficient of O_3 (Clyne and Coxon, 1968) and yielded excellent agreement with other absolute techniques (DeMore and Patapoff, 1976). When NO is present in excess, no side reactions occur and the stoichiometry is as given above. This method has the distinct advantage that it gives an absolute relation among three common pollutants. A measurement of the quantity of NO or O_3 consumed or NO_2 produced provides a simultaneous measurement of the other two species and the GPT procedure has been used in all three modes. This calibration technique is often used in the calibration of chemiluminescence NO_x ($NO + NO_2$) analyzers. In order to obtain accurate concentration measurements in the procedure as normally employed, accurate flow measurements are required; and this is the principal complexity and difficulty with this procedure (DeMore and Patapoff, 1976). Stedman et al. (1976) has employed an appropriate NO detector to make flow ratio measurements and thus avoid the requirement for absolute flow measurements. Because of unexplained biases between GPT measurement systems and the UV reference in the EPA collaborative study, the GPT method was not recommended as an independent calibration technique (Rehme et al., 1981). It is still allowed, however, as a transfer standard in accordance with the EPA guidelines for these standards (McElroy, 1979).

4.2.5 Relationship between Methods for Total Oxidants and Ozone

When the ambient air quality standards for criteria pollutants were originally established, a numerical standard was set for photochemical oxidants as defined by measurements based on iodometric techniques. Much of the health-related and welfare-related evidence used as the basis for the standards was obtained using the total oxidant instrumentation discussed above. The reference method specified in 1971, however, was the chemiluminescence measurement of O_3. Instrumental methods for the specific measurement of atmospheric O_3 became commercially available in 1970. These had several practical advantages over total oxidant KI-based instruments. These advantages were greater sensitivity, precision, specificity--no interferences from ambient SO_2 and NO_2--and improved reliability in routine monitoring. Second, the data available showed that O_3 was the major contributor to total oxidant measurements, that O_3 was the major contributor to observed health and welfare effects, and that O_3 could probably serve, then, as the best surrogate for measurements of total oxidants and for controlling effects of oxidants in ambient air (see reviews in Burton et al., 1976; U.S. Environmental Protection Agency, 1978a).

Notwithstanding the promulgation of standards for ozone rather than photochemical oxidants by EPA in 1979, an examination of the temporal and quantitative relationships between total oxidant and O_3 data remains of considerable interest, largely because earlier data and many newer data on health and welfare effects were obtained by means of total oxidant methods. Aside from the relative paucity of data on simultaneous measurements, there are two distinct problems in making such comparisons. The first is the difficulty in estimating the contributions to the total oxidant measurements from other oxidizing species such as NO_2 and from reducing species such as SO_2. The presence of such species could cause the total oxidant measurements to be either higher or lower than O_3 concentrations. The second difficulty is in estimating the bias created between past and present data as a result of the change from the NBKI to the UV photometry calibration procedures. Fortunately, these two problems can be treated separately and the latter problem vanishes for comparison of simultaneous O_3 and oxidant data obtained using the same calibration procedure.

In the sections below, the relationship that should exist between total oxidant and O_3 is considered from an evaluation of the response of NBKI measurements to other oxidizing and reducing species. The predicted relationship is then compared to data obtained in simultaneous field measurements of total oxidant and O_3.

4.2.5.1 Predicted Relationship. The predicted total oxidant measurements can be expressed as the sum of the contributions from oxidizing and reducing species that release or consume iodine in NBKI reagent:

$$\begin{aligned}[\text{Total Ox}] = {} & a[O_3] + \Sigma_i\, b_i\, [\text{Ox}]_i + c[NO_2] \\ & - d[SO_2] - \Sigma_i\, e_i\, [\text{Red}]_i\end{aligned} \tag{4-6}$$

In this equation, $[\text{Ox}]_i$ and $[\text{Red}]_i$ represent the concentrations of other oxidizing and reducing species in the atmosphere. The atmospheric concentrations of other reducing species, such as H_2S, are normally quite low compared to SO_2 concentrations (Stevens et al., 1972b, and references therein) and these species will not be considered further here. If the concentrations above are true atmospheric concentrations, the constants a, b, c, and d represent the efficiencies with which the various species release or consume iodine. For example, the value of the constant a for an oxidant instrument calibrated by the CARB 2 percent NBKI method would be approximately 1.2 (Section 4.2.4.2). Since the instruments are calibrated with ozonized air, the factor a represents the bias of the calibration method used. If the O_3 concentration is overestimated because of calibration bias, then so are the contributions of the other species by the same factor; i.e., the constants b, c, and d are all higher than their true values by the same constant, a. Therefore, it should in principle be possible to correct total oxidant data for calibration bias by dividing both sides of the equation above by a.

$$\begin{aligned}[\text{Total Ox}]' &= [\text{Total Ox}]/a \\ &= [O_3] + \Sigma_i\, b'_i\, [\text{Ox}]_i + c'[NO_2] - d'[SO_2]\end{aligned} \tag{4-7}$$

Other atmospheric oxidants that have been identified and that may contribute to the total oxidant reading are hydrogen peroxide (H_2O_2), small organic peroxides (e.g., methyl and ethyl hydroperoxide), peracetic acid, peroxyacyl nitrates (Cohen et al., 1967), and pernitric acid (Niki et al., 1976). An estimation of the contribution of these species to the total oxidant measurement is quite difficult because individual b_i's have not been measured and there are few data available on atmospheric concentrations of individual species. The magnitude of the efficiency term will depend not only on the stoichiometry of the oxidation reaction, but also on the rate. A summary of the effects of various oxidants on NBKI reagent and the Mast oxidant meter is given in Table 4-4 (Cohen et al., 1967; Purcell and Cohen, 1967; Burton et al., 1976).

TABLE 4-4. RESPONSE OF NBKI REAGENT AND MAST METER TO VARIOUS OXIDANTS

	NBKI	Mast
Ozone	A[a]	E
Peracetic acid	A	NA[b]
Hydrogen peroxide	B	D
Acetyl peroxide	B	N
Ethyl hydroperoxide	B	NA
_n_-Butyl hydroperoxide	B	NA
tert-Butyl hydroperoxide	B	NA
Nitrogen oxides (NO_x)	D (10% as NO_2)	D (10%)
Peroxyacetyl nitrate (PAN)	D	N
Peroxypropionyl nitrate (PPN)	D	D

[a] A = immediate color development; B = slow color development; D = positive interference; E = good response; and N = no response (or negligible).

[b] NA = Data not available.

Source: Cohen et al. (1967).

By contrast, reaction efficiencies for NO_2 and SO_2 are relatively well known. Tokiwa et al. (1972) observed reaction efficiencies of 6 percent for the Mast oxidant meter, 22 percent for a 10 percent KI colorimetric analyzer, and variable (20 to 32 percent) for a 20 percent KI colorimetric analyzer. It is well documented that SO_2 is a quantitative negative interference with a 100 percent efficiency for reducing the oxidant reading by an amount equivalent to the SO_2 concentration present (Cherniack and Bryan, 1965; Saltzman and Wartburg, 1965).

Returning to the analytical expression for total oxidant, an oxidant value corrected for NO_2 and SO_2 interferences can be expressed as below, assuming that no other significant reducing interferences are present:

$$\begin{aligned}[\text{Total Ox}]_{\text{corr.}} &= [\text{Total Ox}] - c[NO_2] + [SO_2] \qquad (4\text{-}8)\\ &= [O_3] + \Sigma_i\, b_i\, [\text{Ox}]_i\end{aligned}$$

Thus, a total oxidant measurement for which legitimate corrections or compensations for NO_2 and SO_2 have been made should always be higher than a simultaneous O_3 measurement by an amount that is a function of the type and concentrations of other oxidants present. The only major qualifications to this prediction are that both types of measurements must be sampling the same air mass and be calibrated with respect to the same reference; that no other significant reducing interferences are present; and that O_3 losses within sample inlet systems are insignificant. On the other hand, total oxidant data uncorrected for SO_2 and NO_2 interferences may be higher or lower than corresponding O_3 data, depending on the concentrations of these pollutants. Because of the potential presence of these interferences, it is quite difficult or impractical to compare oxidant and O_3 measurements during evening and early morning hours, when O_3 concentrations are quite low. Therefore, in the comparison of total oxidant and O_3 simultaneous field measurements below, emphasis is placed on comparison of peak hourly averages.

4.2.5.2 Empirical Relationship Determined from Simultaneous Measurements. Several precautions should be taken in performing simultaneous measurements. Both kinds of instruments must be calibrated frequently with the same ozonized air stream that has been analyzed by a common reference method. In a simultaneous comparison, daily calibrations should be made with an O_3 generator and the generator output should be analyzed weekly. Both instruments should sample the same air parcel. Routine maintenance should be frequent to ensure constant gas and reagent flow rates, clean sample inlet systems, etc. Finally, in any meaningful comparison of O_3 and oxidant data, simultaneous measurements of NO_2 and SO_2 should be made. If chromium trioxide scrubbers are used to remove SO_2 in the inlet to the oxidant instrument, these must be frequently tested to ensure that O_3 is not also removed during continued use, particularly under very humid conditions. These scrubbers may cause some additional bias by oxidation of NO to NO_2.

The earliest comparative study reported was by Renzetti and Romanovsky (1956). This study compared a phenolphthalein total oxidant monitor, a KI continuous oxidant monitor, a rubber-cracking apparatus, and an open-path ultraviolet spectrometer, which monitored the UV absorption at characteristic O_3 absorption wavelengths. The only meaningful measurements for consideration here are the KI oxidant and UV O_3 measurements, since these are similar to measurement methods used later. The UV O_3 spectrometer differed in a number of respects from the O_3 photometers in use today. Measurements were made across an open optical path of 325 ft of the transmission at three wavelengths, λ_1 = 265 nm, λ_2 = 313 nm, and λ_3 = 280 nm. Intensity ratios at the three wavelengths were used to minimize the effects of other UV absorbers and of particulate scattering. Some non-O_3 absorption may still have been present, and, if so, the measured values would be higher than the true O_3 values. The published absorption coefficients at these three wavelengths were used to compute O_3 concentrations (Vigroux, 1952). Measurements were made over a 4-month period. Figures 4-1 and 4-2 are illustrative of the data obtained for a monthly average and a single day, respectively. Peaks of total oxidant and of O_3 occurred at the same time, but the O_3 maximum was usually less than the total oxidant maximum. The UV O_3 data were usually higher in the wings at low O_3 concentrations. Renzetti and Romanovsky attributed the higher total oxidant reading to the presence of "other oxidants" and estimated concentrations of other oxidants of 0.1 to 0.4 ppm, depending on O_3 concentration. Since the total oxidant instrument was calibrated by an NBKI method, this estimate is almost certainly too high and a large portion of the difference between oxidant and O_3 may have been a result of the 20 to 25 percent positive calibration bias. Since interferences may be present in the UV measurement and simultaneous measurements of NO_2 and SO_2 were not available at the time, no attempt is made to make any more quantitative assessment of this study.

A later study (Cherniack and Bryan, 1965) compared a 10 percent colorimetric KI oxidant instrument, a Mast oxidant meter (Brewer and Milford, 1960), a galvanic-cell oxidant instrument (Hersch and Deuringer, 1963), and a UV O_3 photometer (Bryan and Romanovsky, 1956). This latter instrument was similar in principle to present-day photometers. The precautions noted above were taken. All the instruments were calibrated with respect to the 2 percent UKI calibration procedure used by the LAAPCD. Simultaneous SO_2 and NO_2 measurements were made, but no corrections were made because the concentrations were reported to be quite small during the period of comparison. Atmospheric sampling

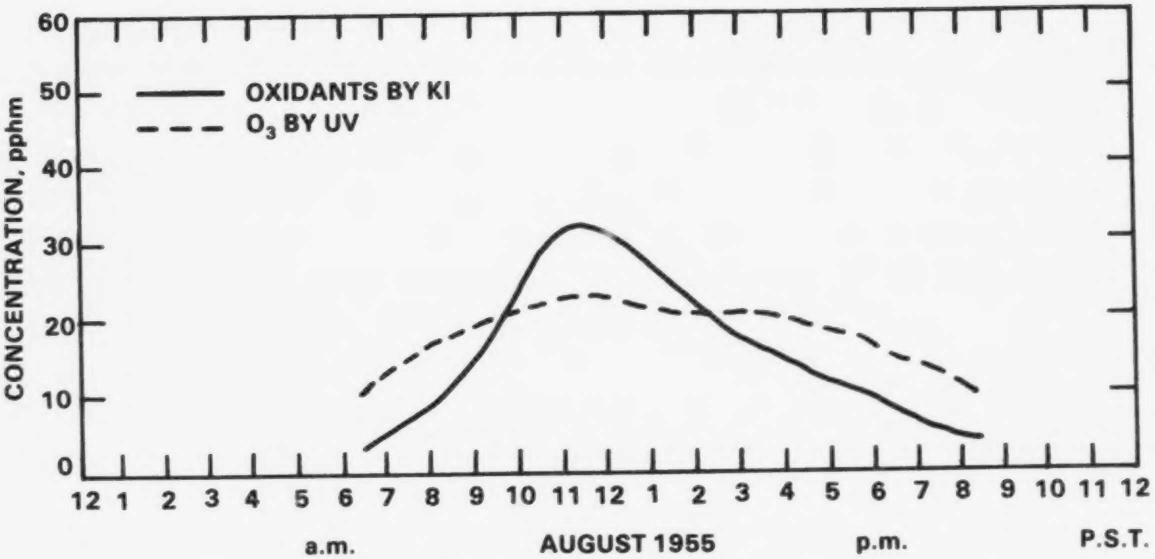


Figure 4-1. Comparison of ozone and total oxidant concentrations in the Pasadena area, August 1955.

Source: Renzetti and Romanovsky (1956).

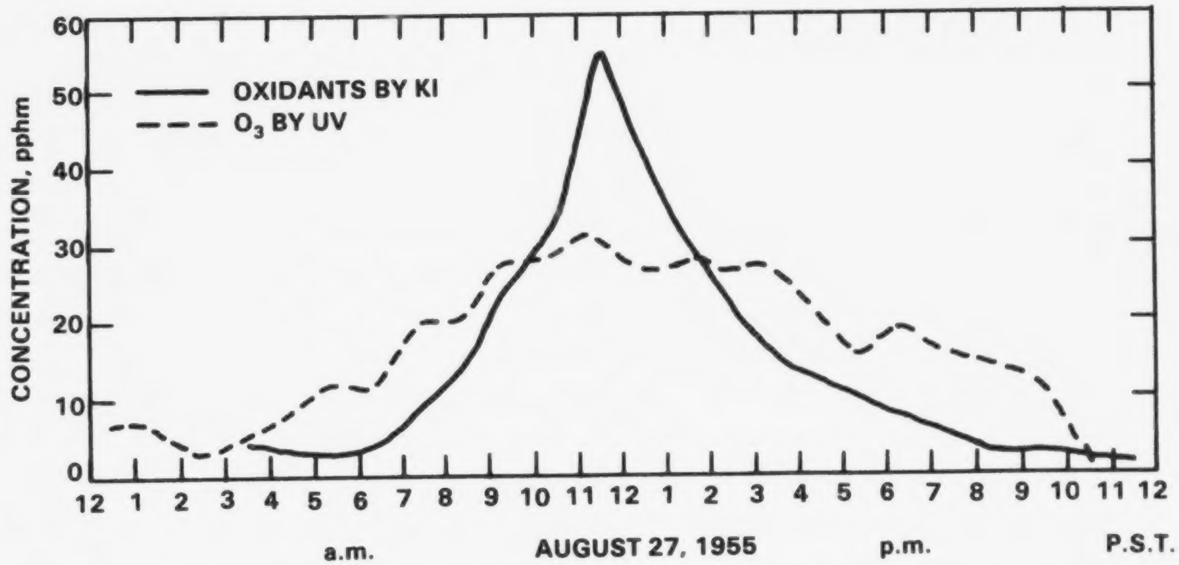


Figure 4-2. Comparison of ozone and total oxidant concentrations in the Los Angeles area, August 1955.

Source: Renzetti and Romanovsky (1956).

was conducted over an unspecified period of time, and the data were referenced to the colorimetric oxidant measurements. The linear regression analysis of the data over the concentration range 0 to 0.6 ppm gave the relationships shown in Table 4-5 after correction for calibration factors. Thus, the data show a much better absolute agreement and correlation between O_3 measurements and colorimetric total oxidant than between electrochemical total oxidant and colorimetric total oxidant. In addition, these data do not indicate any significant contribution by "other oxidants" to the total oxidant measurement.

TABLE 4-5. COMPARISON OF CORRECTED INSTRUMENT READINGS TO COLORIMETRIC OXIDANT READINGS DURING ATMOSPHERIC SAMPLING

Instrument	m	b	r
Mast meter	0.896	-0.013	0.868
Galvanic cell	0.776	+0.004	0.867
Ozone photometer	0.980	-0.005	0.982

(y = Instrument reading
= mx + b; x = colorimetric oxidant measurement; m = slope; b = intercept;
r = correlation coefficient)

Source: Cherniack and Bryan (1965).

During the 1970s, several studies were conducted on the intercomparison of O_3 and total oxidant instrumentation by the Research Triangle Institute (RTI) of North Carolina (Ballard et al., 1971a,b; Stevens et al., 1972a,b). Measurements were made for O_3 by chemiluminescence and for total oxidant by a colorimetric KI analyzer and a Mast meter. Calibrations were carried out Mast meter. Calibrations were carried out frequently with an O_3 generator calibrated by the 1 percent NBKI method. Simultaneous NO_2 and SO_2 measurements were also made and the oxidant data reported were corrected for these interferences. Clark et al. (1974) intercompared a commercial UV photometer, three different commercial gas-phase chemiluminescence analyzers, and a gas-solid chemiluminescence analyzer by monitoring in a rural environment. The instruments were all calibrated by a common reference procedure and hourly-averaged field measurements were collected over a 1-month period in August 1972. Davis and Jensen (1976) reported intercomparisons of Mast meter total oxidant measurements and chemiluminescence O_3 measurements. The instruments were not calibrated by the same procedure, however, nor were any corrections attempted for SO_2 and

NO_2 interferences. Okita and Inugami (1971) reported an intercomparison of KI total oxidant measurements with chemiluminescence O_3 measurements in the urban atmosphere of Musashino, Japan. An intercomparison of total oxidant by KI and O_3 by chemiluminescence in irradiated auto exhaust was reported by Carroll et al. (1972). In another extensive field study conducted at an air monitoring station near the Houston ship channel, Severs and coworkers (Severs, 1975; Neal et al., 1976) examined the relationship between ozone and total oxidants for this area by making simultaneous measurements with a gas-phase chemiluminescence O_3 monitor and a Beckman colorimetric total oxidant analyzer. Primary calibrations of the instruments were performed periodically using the EPA 1 percent NBKI method. No corrections were attempted for NO_2 or SO_2 interferences, but during the latter part of this study a chromium trioxide scrubber was placed in the inlet of the total oxidant analyzer.

All of these 1970 studies were reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1978a). Only the major conclusions are repeated here. In general, the averaged data showed fairly good qualitative and quantitative agreement between the diurnal variations of total oxidants and O_3. The usual trend was a slightly higher value for the total oxidants measurement at the maximum, a not unexpected result in view of the discussion above. Comparisons of monthly-averaged data taken from studies in Los Angeles and St. Louis are shown in Figures 4-3 and 4-4 (Stevens et al., 1972a,b). The total oxidant data shown in Figure 4-4 are uncorrected and show distinct morning and evening peaks resulting from NO_2 interference (see Chapter 3 for diurnal patterns of NO_2). Examination of data taken from individual days shows considerably more variation among the methods, with total oxidant measurements both higher and lower than O_3 measurements. Intercomparisons of only UV photometric and chemiluminescence O_3 analyzers have not shown these large variations (Clark et al., 1974; Wendt, 1975). In all probability, these variations result from the large imprecision and interferences in total oxidant measurement.

Two of the studies described above reported consistently lower total oxidant measurements. In one of these (Davis and Jensen, 1976), the reference KI method was used for calibrating the chemiluminescence analyzer while a factory calibration was used for the Mast meter. As pointed out above, other studies have found low oxidant readings for the Mast meter as compared to colorimetric analyzers (Cherniack and Bryan, 1965; Tokiwa et al., 1972; Stevens et al., 1972a,b). The use of the factory calibration would cause the

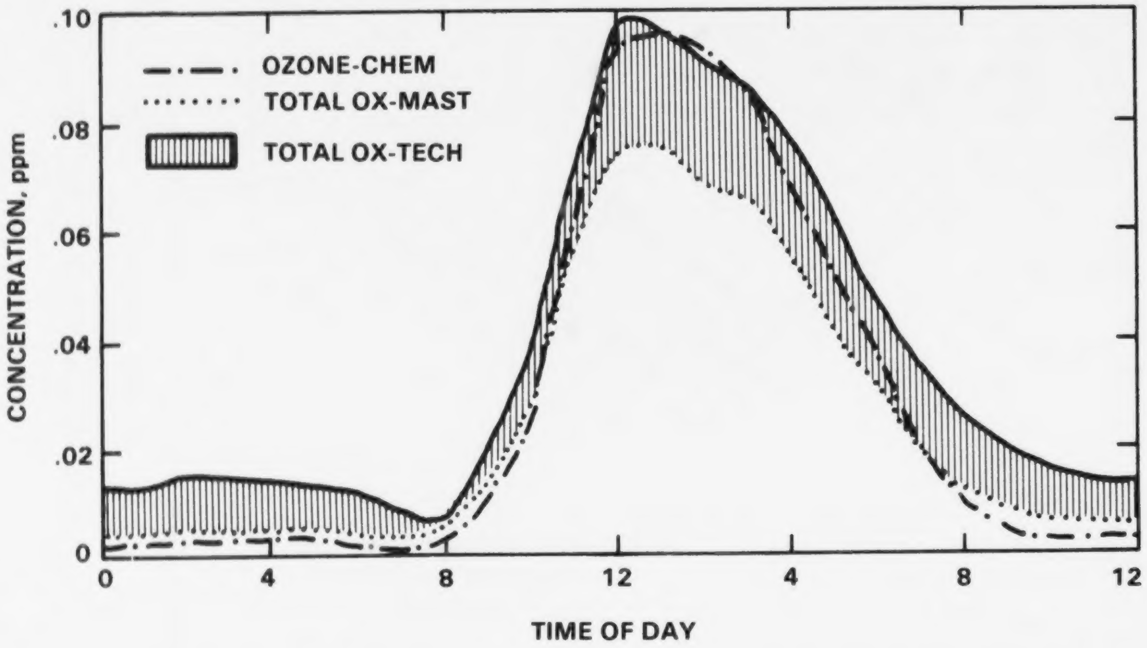


Figure 4-3. Measurements of ozone and total oxidants in Los Angeles, September 4 through September 30, 1971.

Source: Stevens et al. (1972b).

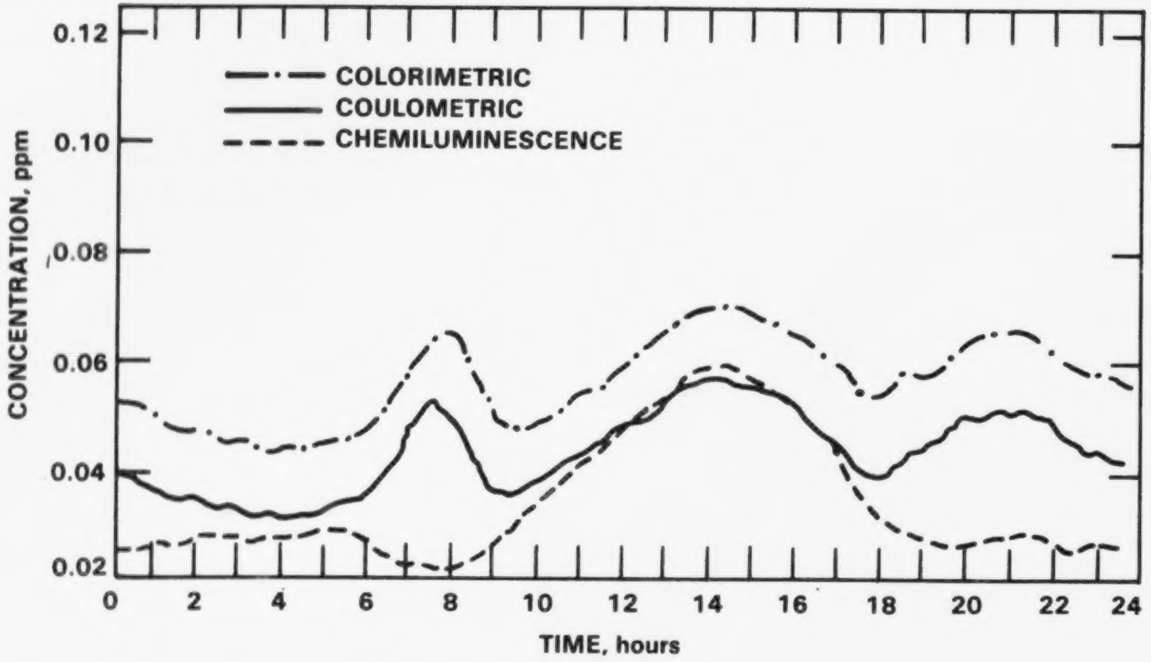


Figure 4-4. Measurements of ozone and total oxidants in St. Louis, October 14 through December 21, 1971.

Source: Stevens et al. (1972a).

Mast readings to be even lower because of a calibration bias (Cherniack and Bryan, 1965; Tokiwa et al., 1972). The results reported by Severs and coworkers are more difficult to evaluate. Chemiluminescence O_3 values generally higher, and sometimes considerably higher, than total oxidant measurements were reported, although the measurements were referenced to the same calibration procedure. Correlations were reported both with and without a chromium trioxide scrubber in the oxidant inlet. These results are inconsistent with the known responses of the instruments and the results of other investigators. The data reported for one day of high O_3, but abnormally low oxidants, are shown in Figure 4-5. It is highly improbable that the problem is with the chemiluminescence O_3 measurement, since this response is typical of a normal O_3 diurnal variation and no other species are known to interfere. It is more probable that some other species of pollutant in the highly industrialized area of the Houston ship channel repressed the response of the total oxidant analyzer, which thus does not respond to O_3, much less to any other oxidant.

The most recent comparison in the literature involved simultaneous O_3 and total oxidant measurements in the Los Angeles basin by the California Air Resources Board (1978) in the years 1974, 1976, and 1978. The maximum hourly data pairs were correlated (Chock et al., 1982) and yielded the following regression equation for 1978 data, in which a large number (927) of data pairs were available:

$$\text{Oxidant (ppm)} = 0.870\ O_3 + 0.005 \qquad (4\text{-}9)$$
$$\text{(correlation coefficient} = 0.92)$$

Thus, when the O_3 levels were relatively high, they were actually slightly higher than total oxidant. The total oxidant data were uncorrected for NO_2 and SO_2 interferences.

In summary, specific O_3 measurements agree fairly well with total oxidant corrected for NO_2 and SO_2 interferences and O_3 is the dominant contributor to total oxidant. Indeed, it is difficult to discern the presence of other oxidants in most total oxidant data. There can, however, be major temporal discrepancies between O_3 and oxidant data, which are primarily a result of oxidizing and reducing interferences with KI measurements. As a result of these interferences, on any given day the total oxidant data may be higher

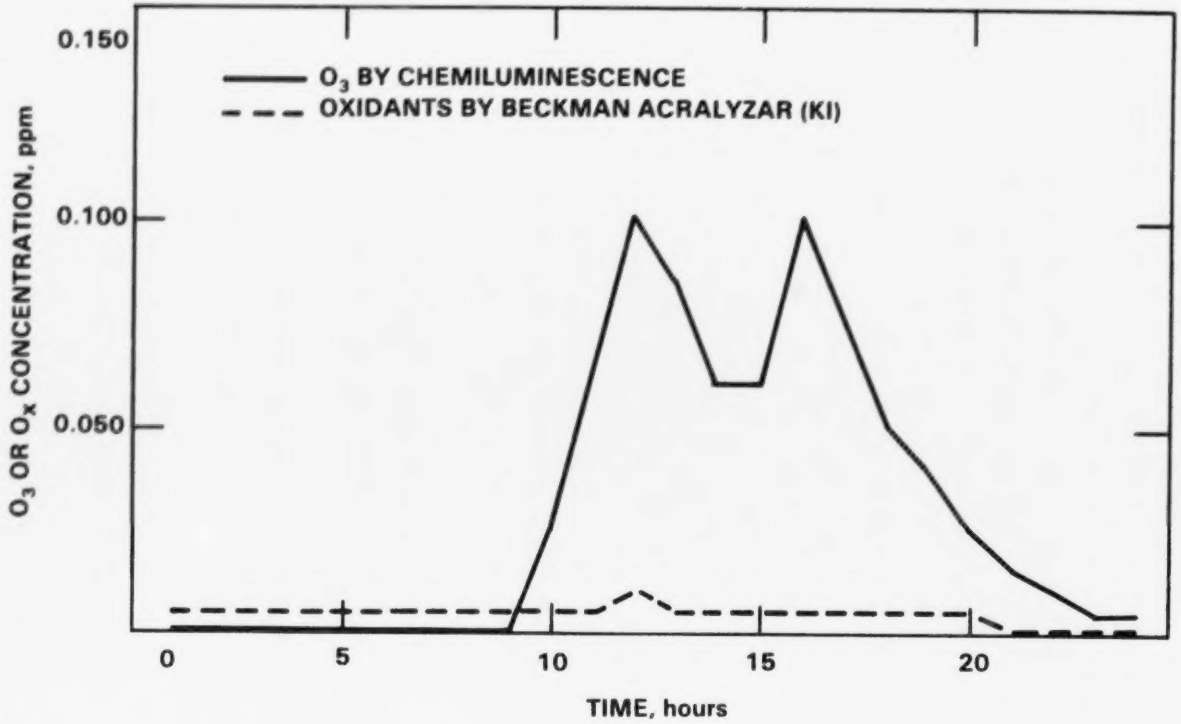


Figure 4-5. Measurements of ozone and total oxidants, Houston Ship Channel, August 11, 1973.

Source: Severs (1975).

than or lower than simultaneous O_3 data. The quantitative relationship between oxidant and O_3 data, such as that used by Chock et al. (1982), is probably quite location-dependent. From a methodologic standpoint, the measurement of O_3 is a more reliable indicator than total oxidant measurements of oxidant air quality, and such difficulties and controversy as may be involved in the intercomparison of O_3 and oxidant measurements are eliminated if the air quality standard is defined in terms of O_3.

4.2.6 Methods for Sampling and Analysis of Peroxyacetyl Nitrate and Its Homologues

4.2.6.1 Introduction. Since the discovery of "compound X" (Stephens et al., 1956a,b), later unambiguously identified as peroxyacetyl nitrate (PAN) (Stephens et al., 1961), much effort has been directed toward its atmospheric measurement. Peroxyacetyl nitrate and its homologues are products of photochemical reactions involving hydrocarbons and oxides of nitrogen (NO_x) in the atmosphere (Stephens et al., 1961). The significance of atmospheric PAN is twofold. It is a potent lachrymator and phytotoxicant in the ppb concentration range (Stephens et al., 1961; Heuss and Glasson, 1968). Because of the reversible thermal equilibrium (Hendry and Kenley, 1977),

$$CH_3O(O_2)NO_2 \leftrightarrows CH_3CO(O_2)\cdot + NO_2, \qquad (4\text{-}10)$$

which is sensitive to the NO_2/NO ratio, PAN may serve as an important reservoir for peroxy radicals and NO_2 (Singh and Salas, 1983a,b) and may play a significant role in both the atmospheric nitrogen cycle and in tropospheric ozone formation (Spicer et al., 1983).

Only two analytical techniques have been used to obtain significant data on ambient PAN concentrations. These are gas chromatography with electron capture detection (GC-ECD) and long-path Fourier-transform infrared (FTIR) spectrometry. Atmospheric data on PAN concentrations have been obtained predominantly by GC-ECD because of its relative simplicity and superior sensitivity. These analytical techniques are described in Section 4.2.6.2 along with attendant methods of sampling. Peroxyacetyl nitrate is somewhat analogous to O_3 in that it is a thermodynamically unstable oxidant and PAN standards must be generated and analyzed by some absolute technique for the purpose of calibrating the GC-ECD. Generation and calibration techniques are discussed separately in Section 4.2.6.3. Finally, the analysis of PAN homologues is discussed briefly in Section 4.2.6.4.

4.2.6.2 Analytical Methods for PAN. By far the most widely used technique for the quantitative determination of ppb concentrations of PAN is GC-ECD (Darley et al., 1963; Stephens, 1969). With Carbowax or SE30 as a stationary phase, PAN can be separated from components such as air, water, and other atmospheric compounds, as well as ethyl nitrate, methyl nitrate, and other contaminants that are present in PAN synthetic mixtures. Electron-capture detection (using a nickel-63 source and a pulsed-current detector or a tritium source and a direct-current detector) provides sensitivity for PAN in the ppb and sub-ppb ranges. A typical column for the separation of PAN would be 3 to 5 feet in length and 1/8 inch in diameter (i.d.), and would be run isothermally at 25° to 60°C. Under these conditions, a peak assignable to PAN appears after 2 to 3 minutes. Table 4-6 shows parameters used by several investigators to determine trace levels of PAN by GC-ECD.

Sample injection into the GC is accomplished by means of a gas-sampling valve with a gas-sampling loop of a few milliliters volume (Stephens and Price, 1973). Sample injection may be performed manually or automatically. Typically, manual air samples are collected in 50 to 200 ml ungreased glass syringes, and purged through the gas-sampling valve. Samples collected from the atmosphere should be analyzed as soon as possible because PAN undergoes thermal decomposition in the gas phase and at the surface of containers. Automatic sample collection and injection may be accomplished by using a small pump to pull ambient air continuously through the sampling loop of an automatic sampling valve, which periodically injects the sample onto the column (Stephens and Price, 1973). Recently, Singh and Salas (1983b) have used cryogenic trapping of PAN, with liquid argon, from relatively large air samples for the purpose of measuring PAN concentrations in the sub-ppb range.

Most of the atmospheric PAN measurements have been made in polluted urban environments, where maximum concentrations of 5 to 50 ppb and average concentrations of a few ppb may occur (Stephens, 1969; Lonneman et al., 1976). For the purpose of such measurements, chromatographic detection limits of 0.1 to 1 ppb are sufficient. The recent work of Singh and Salas (1983a,b) on the measurement of PAN in the free (unpolluted) troposphere is illustrative of current capabilities for measuring low concentrations. A 50- to 200-ml volume of air was collected by preconcentration into an unpacked 0.15 cm o.d. stainless tube of 1.24 ml volume, at liquid argon temperature, prior to analysis (see Table 4-6). For measurements in humid environments, the air sample was passed

TABLE 4-6. SUMMARY OF PARAMETERS USED IN DETERMINATION OF PAN BY GC-ECD

Reference	Column dimensions and materials	Stationary phase	Solid support	Column temperature, °C	Flow rate, (ml/min)	Carrier gas	Elution time, min	Concentration range
Heuss and Glasson, 1968	4 ft x 1/8 in Glass	SE30 (3.8%)	80/100 Mesh Diatoporte S	25	NA[a]	NA	NA	ppb range
Grosjean, 1983	6 ft x 1/8 in Teflon	10% Carbowax 400	60/80 Mesh Chromosorb P	30	40	N_2	NA	ppb range
Darley et al., 1963	3 ft x 1/9 in Glass	5% Carbowax 400	100/200 Mesh Chromosorb W	35	25	N_2	2.17	3 to 5 ppb
Stephens and Price, 1973	1.5 ft x 1/8 in Teflon	5% Carbowax E 400	Chromosorb G 80/100 Mesh treated with dimethyl dichlorosilane	25	60	N_2	1.75	37 ppb
Lonneman et al., 1976	3 to 4 ft x 1/8 in Glass	10% Carbowax 600	Gas Chrom Z	25	70	95% Ar 5% CH_4	2.7	0.1 to 100 ppb
Holdren and Spicer, 1984	5 ft x 1/8 in Teflon	Carbowax 600	60/80 Mesh Gas Chrom Z	35	70	90% Ar 10% CH_4	3.00	ppb range
Peake and Sandhu, 1982	3.3 ft x 1/8 in Glass	5% Carbowax 600	Chromosorb W	33	50	N_2	NA	0.2 to 20 ppb
Singh and Salas, 1983b	1.2 ft x 1/8 in Teflon	10% Carbowax 600	80/100 Mesh Supelcoport	33	30	95% Ar 5% CH_4	NA	0.02 to 0.10 ppb
Grosjean et al., 1984	1.7 ft x 1/8 in Teflon	10% Carbowax 400	60/80 Mesh Chromosorb G	30	40	N_2	5.0	2 to 400 ppb
Nielson et al., 1982	3.9 ft x 1/12 in Glass	5% Carbowax 400	Chromosorb W - AW - DCMS	25	40	N_2	6.0	11 ppb

[a] Not available.

through a Nafion drier (Foulger and Simmonds, 1979) to reduce the humidity prior to preconcentration. A minimum detection limit of 0.01 ppb was obtained. Free tropospheric concentrations in the 0.01 to 0.1 ppb range were always observed and indicated that PAN is a natural constituent of the atmosphere and may constitute a significant fraction of the reactive nitrogen.

There are conflicting reports in the literature on the effects of variable relative humidity on PAN measurements by GC-ECD. In 1973, Stephens and Price stated that in preparing PAN calibration samples "the diluent (gas) should be of normal humidity so that the chromatogram will be a realistic one." Subsequently, Holdren and Rasmussen (1976) observed a reduced response to PAN calibration samples when the relative humidity of the sample was 30 percent or lower and a tenfold decrease in PAN response when the relative humidity approached 0 percent. This effect was attributed to an interaction between sample and GC column. Nieboer and van Ham (1976) reported that "the elution gas stream was previously humidified . . . because it appeared that the height of the PAN peak depends on the relative humidity of ambient air if dry elution gas was used." In contrast to these studies, Lonneman (1977) observed no effect on peak height in PAN calibration samples in which the relative humidity varied from 10 to 50 percent.

In 1978, Watanabe and Stephens reported on a reexamination of the moisture anomaly and investigated the effects of humidity on PAN storage flasks, columns, and detectors. A consistent PAN loss to the walls of dry acid-washed glass storage flasks was observed, but the PAN could be recovered by the addition of moisture to the flasks. A tritium direct-current detector showed no humidity effect except for a small (5 to 10 percent) decrease in peak height in a few cases at very low humidities (2 to 3 percent). With a different GC instrument employing a Ni-63 detector, erratic responses were observed at low humidities, with responses reduced 30 to 95 percent from that obtained at 53 percent relative humidity. No conclusion was drawn on whether this difference reflected a humidity effect on the detector, the column, or the sampling value. Finally, the moisture anomaly did not appear to depend on column history or loading even after a bake-out treatment.

In the most recent study (Grosjean et al., 1984), the humidity effect on PAN calibration samples prepared by the dynamic and static irradiation of $CH_3CHO-Cl_2-NO_2$ mixtures was examined. A small decrease ($\leq$3 percent) was observed in PAN peak height when the dry air stream was passed either over an impinger containing water or directed through the water impinger. These results are in contradiction to all of the above, in which the response to humidified PAN samples is either greater than or the same as dry PAN samples.

It is noteworthy that the chromatographic systems employed by different investigators often employ different materials (e.g., glass, Teflon, stainless steel), column loadings, and detectors. The resolution of all the differences noted above in regard to a suspected humidity effect might require considerable effort. For the present, if a moisture effect is suspected in a PAN analysis, the bulk of this evidence suggests that humidification of PAN calibration samples (to a range approximating the humidity of the samples being analyzed) would be advisable.

Conventional long-path infrared spectroscopy and Fourier-transform infrared spectroscopy (FTIR) have been used to detect and measure atmospheric PAN. Sensitivity is enhanced by the use of FTIR over conventional long-path infrared spectroscopy. Accurate knowledge of the absorptivities of many IR bands assignable to PAN makes possible the quantitative analysis of PAN without the use of calibration standards. The most frequently used IR bands have been assigned and the absorptivities shown in Table 4-7 have been reported. Only the key bands are shown, but all 27 fundamentals are infrared active and Bruckmann and Willner (1983) have assigned most of them. The assignment by Adamson and Guenthard (1980) of the bands at 1435, 1300, and 990 cm^{-1} to an impurity, CH_3ONO_2, is apparently incorrect. Bruckmann and Willner (1983) observed these same bands in a 99 percent pure PAN sample.

The initial discovery of PAN in simulated photochemical smog was accomplished by long-path infrared absorption spectrometry (Stephens et al., 1956b). Some recent simultaneous measurements of PAN and other atmospheric pollutants such as O_3, HNO_3, HCOOH, and HCHO have been made by long-path FTIR spectrometry during smog episodes in the Los Angeles Basin. Tuazon et al. (1978) have described an FTIR system operable at pathlengths up to 2 km for ambient measurements of PAN and their trace constituents. This system employed an eight-mirror multiple reflection cell with a 22.5-m base path. The spectral windows available at pathlengths of 1 km were 760-1300, 2000-2230, and 2390-3000 cm^{-1}. Thus, PAN could be detected by the bands at 793 and 1162 cm^{-1}. The 793 cm^{-1} band is characteristic of peroxynitrates, while the 1162 cm^{-1} band is reportedly caused by PAN only (Stephens, 1969; Hanst et al., 1982). Tuazon et al. (1981a,b) reported ambient measurements with this system during a smog episode in Claremont, CA, in 1978. Maximum PAN concentrations ranged from 6 to 37 ppb over a 5-day episode; the report presented diurnal patterns for PAN and several

TABLE 4-7. INFRARED ABSORPTIVITIES OF PEROXYACETYL NITRATE (BASE 10)

	Vapor ppm^{-1}m^{-1} x 10^4				Solution in n-octane, µm^{-1} (µg/µL)$^{-1}$	
Mode	Frequency, cm^{-1}	0.1 m, no diluent (Bruckmann and Willner, 1983)[a]	0.1 m path; N_2 at ~1 atm (Stephens, 1964)[b]	120 m path; air at ~1 atm (Stephens, 1964)[b]	Frequency, cm^{-1}	(Holdren and Spicer, 1984)
v(c=0)	1842	12.4	10.0	NA[c]	1830	0.00041
$v_{as}(NO_2)$	1741	32.6[d]	23.6	NA	1728	0.00115
$v_s(NO_2)$	1302	13.6	11.2	11.4	1294	0.00041
v(c-o)	1162.5	15.8	14.3	13.9	1153	0.00042
v(o-o)	930	NA	1.8	NA	NA	NA
$\delta(NO_2)$	791.5	13.4	10.1	10.3	787	0.00044

[a] FTIR spectra 1-1.2 cm^{-1} resolution.

[b] Prism spectra ~10 cm^{-1} resolution.

[c] NA = Data not available.

[d] Resolved Q branch.

other pollutants for the 2 most severe days. The detection limit given for PAN at a 900-m pathlength was 3 ppb.

Hanst et al. (1982) modified the FTIR system used by Tuazon et al. (1978) by changing it from an eight-mirror to a three-mirror cell configuration and by considerably reducing the cell volume. Measurements were made over a 1260-m optical path folded along a 23-m base path at 0.25 cm^{-1} resolution. Measurements were reported for PAN and a variety of other pollutants for a 2-day smog episode at California State University, Los Angeles, in 1980. The maximum PAN concentration observed was 15 ppb for this period of only moderate smog intensity. An upper limit of 1 ppb of peroxybenzoyl nitrate (PbzN) was placed based on observations in the vicinity of the PBzN band at 990 cm^{-1}. The reports by Tuazon et al. (1978) and Hanst et al. (1982) both refer to earlier FTIR ambient air studies.

Sampling may constitute one of the major problems in the analysis of trace reactive species, such as PAN, by long-path FTIR spectrometry. The folded-path White cells have a large internal volume (15 m^3 for Tuazon et al., 1978; 3 m^3 for Hanst et al., 1982). The large internal surface area may serve to promote the decomposition or irreversible adsorption of reactive trace species. To minimize these effects, both Tuazon et al. and Hanst et al. employed high-speed blowers to pull ambient air through the cells at high velocities. For interior cell linings, Hanst et al. employed 0.5 mm polyvinyl chloride sheeting and Tuazon et al. used Plexiglas and FEP Teflon.

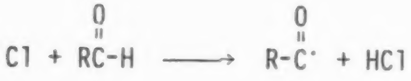
Pitts et al. (1973) proposed a chemiluminescence technique for continuous monitoring of ambient concentrations of PAN. The reactions of both PAN and O_3 with triethylamine in the gas phase produce chemiluminescence. The spectra reported overlap somewhat with a λ_{max} of 520 nm for the O_3 reaction and λ_{max} of 650 nm for the PAN reaction. Pitts proposed a technique that included the measurement of the emission intensity in the two regions by the use of optical cut-off filters. Thus, the PAN concentration can be determined, provided the absolute O_3 concentration is simultaneously measured. Concentrations of 6 ppb PAN were detected and a lower limit of detection of 1 ppb was estimated. No interfering emissions were observed from methyl nitrate, ethyl nitrate, ethyl nitrite, or NO_2. No further work has been reported on the development of this technique, and there have been no atmospheric applications.

4.2.6.3 Generation and Calibration of PAN. Because of the thermal instability of dilute PAN samples and the explosive nature of liquid PAN, calibration samples are not commercially available; each laboratory involved in making such measurements must prepare its own standards. The PAN samples are prepared by various means at concentrations in the ppm range and these must be analyzed by some absolute technique. The analyzed samples must then be diluted to obtain gas-phase samples in the low ppb range for direct calibration of GC instruments. Thus, this section includes descriptions of various means of PAN generation, methods of analysis, and the procedures for sample handling and storage where applicable.

The earlier methods used for the preparation of PAN have been summarized by Stephens (1969). These included (1) the photolysis of mixtures of nitrogen oxides with organic compounds in air or oxygen (Stephens et al., 1956b; Stephens et al., 1961); (2) the photolysis of alkyl nitrite vapor in oxygen (Stephens et al., 1965); (3) the dark reaction of aldehyde vapor with nitrogen pentoxide (Tuesday, 1961); and (4) the nitration of peracetic acid. Of these methods, the photolysis of alkyl nitrites was favored and used extensively by Stephens and other investigators. As described by Stephens et al. (1965), the liquefied crude mixture obtained at the outlet of the photolysis chamber is purified by preparation-scale GC. [CAUTION: Both the liquid crude mixture and the purified PAN samples are violently explosive and should be handled behind explosion shields using plastic full-face protection, gloves, and a leather coat at all times. These PAN samples should be handled in the frozen or gaseous state whenever possible.] The pure PAN is usually diluted to about 1000 ppm in cylinders pressurized with nitrogen to approximately 100 psig. When refrigerated at ≤15°C, PAN losses are less than 5 percent per month (Stephens et al., 1965). Lonneman et al. (1976) used the photolysis products without purification for the calibration of GC instruments in the field and discussed the use of Tedlar bags for the preparation and transport of calibration samples.

Gay et al. (1976) have used the photolysis of Cl_2: aldehyde: NO_2 mixtures in air or oxygen for the preparation of PAN and a number of its homologues at high yields:

$$Cl_2 + h\nu \longrightarrow 2\ Cl \qquad (4\text{-}11)$$



$$Cl + R\overset{O}{\overset{\|}{C}}{-}H \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{\cdot} + HCl \qquad (4\text{-}12)$$

$$R\overset{O}{\overset{\|}{C}}{}^{\cdot} + O_2 + M \longrightarrow R\overset{O}{\overset{\|}{C}}-O_2{}^{\cdot} + M \tag{4-13}$$

$$R\overset{O}{\overset{\|}{C}}-O_2{}^{\cdot} + NO_2 \longrightarrow R\overset{O}{\overset{\|}{C}}-O_2-NO_2 \tag{4-14}$$

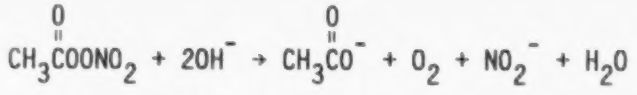
This procedure has been utilized in a portable PAN generator that can be used for the calibration of GC-ECD instruments in the field (Grosjean, 1983; Grosjean et al., 1984). The output of this generator is a dynamic flow of PAN in air at a concentration of about 2 to 450 ppb. Dilute concentrations of reactant gases for the photolysis chamber are obtained by passing a controlled flow of air over Cl_2, NO_2, and acetaldehyde permeation tubes.

The other technique for PAN preparation in current use involves the nitration of peracetic acid. In the 1969 review (Stephens, 1969), this approach was considered not useful for synthesis. Several investigators, however, have recently reported on a condensed-phase synthesis of PAN with peracetic acid that produces high yields of a pure product free of other alkyl nitrates (Hendry and Kenley, 1977; Kravetz et al., 1980; Nielsen et al., 1982; Holdren and Spicer, 1984). Most of these procedures call for the addition of peracetic acid (40 percent in acetic acid) to a hydrocarbon solvent (pentane, heptane, octane) maintained at -80°C in a dry-ice acetone bath, followed by acidification with sulfuric acid. Nitric acid is formed in situ with stirring by the slow addition of sodium nitrate. After the nitration is complete, the hydrocarbon fraction, containing PAN concentrations of 2 to 4 mg/ml (Nielsen et al., 1982), can be stored at -20°C for periods longer than a year (Holdren and Spicer, 1984). After analysis, the PAN-hydrocarbon solutions can be used directly for calibration by the evaporation of measured microliter volumes of solution into Tedlar bags containing known volumes of clean air.

The most direct method for absolute analysis is by infrared absorption using absorptivities given in Table 4-7. This is the technique used by Stephens (1969; analysis of PAN in N_2 cylinders), Lonneman et al. (1976; analysis of gas-phase products from photolysis of ethyl nitrite); and Holdren and Spicer (1984; analysis of PAN in octane solutions). Whereas long, folded-path cells and FTIR spectrometry are required for the analysis of atmospheric PAN, conventional IR instruments and 10-cm gas cells can analyze gas standards with concentrations greater than 35 ppm (Stephens, 1969) and Holdren and Spicer

(1984) used 50-μm liquid microcells for the analysis of PAN in octane solutions. Another candidate technique for absolute PAN analysis was gas-phase coulometry using a tandem electron-capture detector (Lovelock et al., 1971). Singh and Salas (1983b) have shown, however, that this technique is unsuitable for absolute PAN analysis because a significant fraction of the PAN is destroyed prior to coulometric detection.

The alkaline hydrolysis of PAN to acetate ion and nitrite ion in quantitative yield (Nicksic et al., 1967) provides a means independent of infrared for the quantitative analysis of PAN. Molecular oxygen is also produced in quantitative yield by the reaction (Stephens, 1967):



$$CH_3\overset{O}{\overset{\|}{C}}OONO_2 + 2OH^- \rightarrow CH_3\overset{O}{\overset{\|}{C}}O^- + O_2 + NO_2^- + H_2O \qquad (4\text{-}15)$$

The colorimetric determination of nitrite ion with Saltzman reagent was first used to measure PAN quantitatively (Nicksic et al., 1967; Stephens, 1969; Kravetz et al., 1980). Nielsen et al. (1982) analyzed the hydrolyzed products of pure PAN samples by ion chromatography for nitrite and nitrate and found that 4 percent of the nitrite had been oxidized to nitrate. Some gas-phase PAN calibration samples (e.g., photolysis of Cl_2: acetaldehyde: NO_2) contain impurities such as NO_2 that will yield nitrite and nitrate in aqueous solution. Thus, Grosjean (1983) and Grosjean et al. (1984) performed ion chromatographic analysis of the acetate ion to determine the PAN output of a portable generator.

An alternate calibration procedure has been proposed based on the thermal decomposition of PAN in the presence of excess NO, and measurement by chemiluminescence of the NO consumed (Lonneman et al., 1982). The acetylperoxy radical, $CH_3C(O)O_2$, and its decomposition products rapidly oxidize NO to NO_2. In the presence of a small amount of benzaldehyde, which is used to scavenge the hydroxyl radical and control the stoichiometry, simulation models predict that 5 molecules of NO will be removed per PAN molecule present. By the use of NO and PAN standard mixtures and the chemiluminescent measurement of the NO consumed, the experimental value was determined to be $\Delta NO/\Delta PAN = 4.7 \pm 0.2$. This measurement could be performed in field stations where chemiluminescent NO analyzers are usually available.

4.2.6.4 Methods of Analysis of Higher Homologues. The GC-ECD analyzer is likewise used for the higher homologues of PAN (Darley et al., 1963; Stephens, 1969; Heuss and Glasson, 1968). The higher homologues elute with longer retention times. The first observation of peroxypropionyl nitrate (PPN) in heavily polluted air was by Darley et al. (1963), who also measured peroxybutyryl (PBN) nitrate in synthetic mixtures by GC-ECD. The concentrations of the higher homologues in ambient air are usually below the detection limits of the GC-ECD technique. Heuss and Glasson (1968) measured peroxybenzoyl nitrate (PBzN) in irradiated auto exhaust samples by GC-ECD and reported that this homologue was 100 times more potent than PAN as a lachrymator. The direct analysis of PBzN by GC-ECD is reported to be complicated by interferences (Appel, 1973). Therefore, an analytical technique was developed in which the PBzN was quantitatively hydrolyzed to methyl benzoate (MeOBz), followed by GC analysis for MeOBz using a flame ionization detector (Appel, 1973). An upper limit of 0.07 ppb was placed on the concentration of PBzN in the San Francisco bay area. The analysis for the higher homologues of PAN in the atmosphere by FTIR spectrometry is not feasible because of inadequate sensitivity, although Hanst et al. (1982) placed an upper limit for PBzN in smoggy Los Angeles air of 1 ppb based on absorption in the 990 cm^{-1} region.

The higher homologues of PAN may be prepared for use in calibration in the same manner as PAN by the use of a compound containing the parent alkyl group. Thus, PPN and PBzN have been prepared by the photolysis of alkyl nitrates in oxygen (Stephens, 1969) and parent aldehydes plus chlorine and NO_2 (Gay et al., 1976). The study of Gay et al. (1976) confirmed that the first member of the series, peroxyformyl nitrate [$HC(O)O_2NO_2$], is too unstable to be observed. There have been few reports of the absolute analyses for the higher homologues. Infrared absorption analysis of purified samples should be the preferred technique. Infrared absorptivities of homologues have been reported by Stephens (1969) and Gay et al. (1976).

4.2.7 Methods for Sampling and Analysis of Hydrogen Peroxide

4.2.7.1 Introduction. Hydrogen peroxide (H_2O_2) is mechanistically significant in photochemical smog as a chain terminator and as an index of the hydroperoxyl radical (HO_2) concentration (Bufalini and Brubaker, 1969; Demerjian et al., 1974). The major reaction leading to the formation of H_2O_2 is the recombination of the hydroperoxyl radical (Graedel et al., 1976):

$$HO_2^{\cdot} + HO_2^{\cdot} + M \rightarrow H_2O_2 + O_2 + M \qquad (4\text{-}16)$$

Recent studies have implicated atmospheric H_2O_2 in the aqueous-phase oxidation of SO_2 to SO_4^{-2} and in the acidification of rain (Penkett et al., 1979; Dasgupta, 1980a,b; Martin and Damschen, 1981; Overton and Durham, 1982).

One of the major problems in assessing the role of atmospheric H_2O_2 has been a lack of adequate measurement methodology. Earlier measurements for atmospheric H_2O_2 were by the titanium colorimetric method (Gay and Bufalini, 1972a,b; Bufalini et al., 1972) and by a chemiluminescence technique (Kok et al., 1978a,b). The reported H_2O_2 concentrations (0.01 to 0.18 ppm) are now believed to be far too high, primarily as a result of artifact H_2O_2 formation from reactions of absorbed O_3 (Zika and Saltzman, 1982; Heikes et al., 1982; Heikes, 1984). Furthermore, maximum tropospheric H_2O_2 concentrations predicted by modeling calculations (Chameides and Tan, 1981; Logan et al., 1981) and observed in recent field studies (Das et al., 1983) are on the order of 1 ppb. In a recent study, a chemiluminescence technique was employed with an argon sample purge to remove O_3 interference, and a maximum H_2O_2 concentration of 1.2 ppb was observed in a polluted urban environment (Das et al., 1983). Promising techniques that have been used or proposed for aqueous- and gas-phase H_2O_2 are discussed below, as well as methods for sampling, generation, and standardization of H_2O_2 samples.

4.2.7.2 Sampling. Almost all of the methods used for the measurement of atmospheric H_2O_2 have used aqueous traps for sampling. Midget impingers (Gay and Bufalini, 1972a,b; Kok et al., 1978b; Das et al., 1983), continuous extractors (Kok et al., 1978a), and gas washing traps (Zika and Saltzman, 1982) have been used. Aqueous traps have been found to be highly efficient in removing trace concentrations of H_2O_2 from gas streams (Zika and Saltzman, 1982). Atmospheric O_3, however, which is also absorbed at concentrations much higher than H_2O_2, reacts in the bulk aqueous phase and at surfaces to produce H_2O_2 and thus is a serious interference (Zika and Saltzman, 1982; Heikes et al., 1982; Heikes, 1984). Details of the aqueous chemistry of O_3 can also be found in other sources (Hoigne and Bader, 1976; Kilpatrick et al., 1955; Taube and Bray, 1940). Because the rate of H_2O_2 production is relatively slow (Heikes, 1984), the removal of absorbed O_3 by purging immediately after sample collection may remove or substantially reduce this interference. This was the approach employed by Zika and Saltzman (1982) and by Das et al. (1983). Another problem identified with aqueous sampling is that other atmospheric species (in particular, SO_2) may interfere with the generation of H_2O_2 in aqueous traps and also react with collected H_2O_2 to reduce the apparent H_2O_2 concentration measured (Heikes et al., 1982).

4.2.7.3 Measurement. A number of methods for measuring low levels of H_2O_2 have been reported, including the following:

1. Titanium colorimetric methods.
2. Chemiluminescence methods.
3. Enzyme-catalyzed methods.
4. Laser diode infrared method.
5. Fourier-transform infrared method (Niki et al., 1980; Hanst et al., 1975, 1982).
6. Electrochemical methods (Pisarevskii et al., 1980).
7. H_2O_2-olefin reaction (Hauser and Kolar, 1968).
8. Mixed-ligand complexes (Csanyi, 1981; Meloan et al., 1961).
9. Iodometry.

Of these techniques, only the chemiluminescence and enzyme-catalyzed methods are summarized below. A summary of methods reported in the literature is given in Table 4-8. Although titanium colorimetric methods have been applied in atmospheric measurements, these techniques are now thought to have inadequate sensitivity for the actual atmospheric concentrations that are present. In addition, these techniques have questionable specificity. The same comments apply to methods 6 through 8 and only the primary references are given above for those methods. At the present state-of-art, the inevitable presence of water vapor absorption limits the use of Fourier-transform infrared methods to concentrations above about 0.040 ppm (Hanst et al., 1982). The use of a tunable diode infrared laser source should eliminate the problem associated with nearby water bands, and this method is currently under investigation for atmospheric measurements (unpublished work in progress, Schiff, 1985). Iodometric techniques are useful only for calibration of H_2O_2 standards and will be discussed in that section.

4.2.7.3.1 Chemiluminescence. Hydrogen peroxide in the atmosphere may be detected at low concentrations by the chemiluminescence obtained from Cu(II)-catalyzed oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) by H_2O_2 (Armstrong and Humphreys, 1965; Kok et al., 1978a,b). The reagent is a solution containing NaOH (pH = 12.8) and luminol, 10^{-5} M Cu(II). The products of the reaction with H_2O_2 are 3-amino-phthalic acid, a nitrogen molecule, and

TABLE 4-8. MEASUREMENT METHODS FOR HYDROGEN PEROXIDE

Method	Reagent(s)	Limits of detection[a]	Interferences[b]		Applications	Primary reference
			Positive	Negative		
Titanium colorimetry	(1) Titanium Sulfate -8-Quinolinol (2) Titanium Tetrachloride	(1) 1.6×10^{-6} M (2) ca 10^{-6} M	Alkyl hydroperoxides	SO_2[c]	Atmospheric	(1) Gay and Bufalini (1972a,b) (2) Pilz and Johann (1974); Kok et al. (1978a)
Chemiluminescence	Luminol, Cu(II) basic solution	0.001 to 1 ppm	PAN[d]	SO_2	Atmospheric, rainwater	Armstrong and Humphreys (1965); Kok et al. (1978a,b)
Enzyme-catalyzed	Scopoletin, horseradish-peroxidase (HRP)	1.5×10^{-11} M	NA	NA	Atmospheric, rainwater	Andreae (1955); Perschke and Broda (1961); Zika and Saltzman (1982)
Enzyme-catalyzed	Leuco crystal violet, HRP	10^{-8} M	NA	NA	---	Mottola et al. (1970)
Enzyme-catalyzed	3-(p-hydroxyphenyl) propionic acid	10^{-6} to 10^{-4} M[e]	NA	NA	---	Zaitsu and Okhura (1980)
Fourier-transform infrared absorption	None	0.040 ppm (est.)	NA[f]	None	Atmospheric[g]	Hanst et al. (1982)
Electrochemical	Aqueous solutions	5×10^{-6} to 1 M	NA	NA	---	Pisarevskii et al. (1980)
H_2O_2-olefin reactions	1,2-di-(4-pyridyl) ethylene	10^{-6} to 5×10^{-4} M	O_3	NA	---	Hauser and Kolar (1968)
Mixed-ligand complex reagents	Vanadium and uranium hydroxamic acid chelates	10^{-6} M	NA	NA	---	Csanyi (1981); Meloan et al. (1961)

[a] Except where noted, detection limits are in moles/liter(M) in aqueous solution.

[b] O_3 is an interference in all these procedures using aqueous sampling. See Text. NA = not available.

[c] The SO_2 interference is reported to be small at high SO_2 concentrations (Gay and Bufalini, 1972b). Studies of potential positive and negative interferences are incomplete for these methods.

[d] The reported PAN interference is small (Kok et al., 1978b).

[e] The lower limit could presumably be reduced by the use of larger samples.

[f] With sufficient resolution, there should be no interferences. IR absorption by atmospheric water vapor is the major analytical limitation.

[g] H_2O_2 bands have not been observed in any long-path FTIR studies. The estimated lower limit of detection in these studies is approximately 0.04 ppm.

a photon of light at 450 nm. The detection limit for atmospheric samples was given as 0.001 ppm, and the linear dynamic range is 0.001 to 1 ppm. This technique as initially employed suffered the interferences from O_3 and SO_2 discussed above for aqueous traps. Das et al. (1982) employed a static version of the method of Kok et al. (1978a) to measure H_2O_2 concentrations in the 0.01 to 1 ppb range. In addition, samples were purged with argon immediately after collection to eliminate, reportedly, the O_3 interference.

Recently, a modified chemiluminescence method has been reported that used hemin, a blood component, as a catalyst for the luminol-based H_2O_2 oxidation (Yoshizumi et al., 1984). This method was applied to the measurement of H_2O_2 in rainwater. There was no interference for SO_2 but a significant positive O_3 interference was reported.

4.2.7.3.2 Enzyme-Catalyzed Methods (Peroxidase). This general method involves three components: a substrate that is oxidizable; the enzyme, horseradish peroxidase (HRP); and H_2O_2. The production or decay of the fluorescence intensity of the substrate or reaction product is measured as it is oxidized by H_2O_2, catalyzed by HRP. Some of the more widely used chromogenic substrates have been scopoletin (6-methoxy-7-hydroxy-1,2-benzopyrone) (Andreae, 1955; Perschke and Broda, 1961); 3-(p-hydroxyphenyl)propionic acid (HPPA) (Zaitsu and Okhura, 1980); and leuco crystal violet (LCV) (Mottola et al., 1970).

In the scopoletin method, the reagent solution is mixed with a second solution containing the H_2O_2, the concentration of which must not be less than 0.33 nor more than 0.84 times the concentration of scopoletin (Perschke and Broda, 1961). The disappearance of scopoletin fluorescence is monitored and the fluorescence intensity can be used to obtain the concentration of H_2O_2 from a calibration curve. The most significant advantages of this method of analysis are the specificity for H_2O_2, the sensitivity, and the stoichiometry of the scopoletin:H_2O_2 reaction (1:1 mole per mole as long as scopoletin is present in a 20-fold excess over HRP). The chief disadvantage of the scopoletin method is that the concentration of H_2O_2 must be within a narrow range in order to obtain an accurately measurable decrease in fluorescence. This limits the usefulness of the technique in determining unknown H_2O_2 concentrations over several orders of magnitude (Armstrong and Humphreys, 1965; Andreae, 1955). Detection limits for this technique are quite low and are in the range of 1.5×10^{-11} M (Perschke and Broda, 1961) to 2×10^{-10} M (Andreae, 1955). This technique has been applied to measurements of H_2O_2 in rainwater by Zika and Saltzman (1982).

With the leuco crystal violet (LCV) substrate, intensely colored crystal violet is formed from the reaction of H_2O_2 with LCV, catalyzed by HRP (Mottola et al., 1970). The absorbance is measured at 596 nm, where the absorption coefficient of crystal violet is 10^5 $M^{-1}cm^{-1}$, a very high value and an inherent advantage of this method. The concentration of H_2O_2 is a linear function of the concentration of crystal violet produced. The detection limit reported is about 10^{-8} M H_2O_2 for an absorbance of 0.005 in a 5-cm cell.

The HRP catalyzes the oxidation of a wide variety of hydrogen-donating substrates by H_2O_2. Zaitsu and Okhura (1980) have tested a number of 4-hydroxyphenyl compounds and found that 3-(p-hydroxyphenyl) propionic acid (HPPA) provided the most sensitive and rapid means for determining H_2O_2. When HPPA reagent solution is mixed with HRP solution and a test solution containing H_2O_2, a product is formed that fluoresces at 404 nm following excitation at 320 nm. The intensity of this fluorescence is monitored as a function of H_2O_2 concentration. The detection limit was reported to be 10^{-10} mole H_2O_2 with a linear range extending to 10^{-8} mole H_2O_2 when a test solution of only 0.1 ml volume was used. Presumably the molar sensitivity could be improved by the use of larger sample volumes. No interference studies were reported. More recently, the acetic acid homologue of HPPA has been employed (Kunen et al., 1983; Dasgupta and Hwang, 1985). The fluorescence intensity of the product dimer is directly proportional to H_2O_2 concentration.

The enzymatic methods appear to be the most promising aqueous, colorimetric methods for H_2O_2 and have considerably greater sensitivity than other colorimetric methods. Studies of potential atmospheric interferences, however, have not been reported for any of these three substrates.

4.2.7.4 Generation and Calibration Methods

4.2.7.4.1 Generation. Standard samples containing trace concentrations of H_2O_2 are required for testing and calibration of various measurement methodologies. As with O_3, such standards are not available and are usually prepared at the time of use. A number of techniques have been employed for generating aqueous standards, but convenient methods for the generation of gas-phase standards are noticeably lacking.

Techniques for the generation of high concentrations of H_2O_2 have been discussed by Shanley (1951). Commercial solutions of 30 percent aqueous H_2O_2 are readily available. Trace levels of H_2O_2 in water may be generated by the irradiation of water with ^{60}CO γ-radiation (Hochanadel, 1952; Armstrong and Humphreys, 1965) and by enzymatic means (Andreae, 1955). By far the most convenient method for generating aqueous standards containing micromolar concentrations of H_2O_2 is simply the serial dilution of commercial-grade 30 percent H_2O_2 (Fisher Analytical Reagent). Samples prepared in this manner must be standardized and the method usually employed is the iodometric technique discussed below. Stock standard solutions of H_2O_2 as low in concentration as 10^{-4} M have been found to be stable for many weeks if kept in the dark (Armstrong and Humphreys, 1965).

Techniques for the convenient generation of gas-phase standards are not available. With the increased interest in atmospheric H_2O_2, there is an obvious need for an H_2O_2 generator comparable to the photolytic O_3 generator discussed in Section 4.2.4.1. A technique that has often been used for generating ppm concentration levels of H_2O_2 in air has been described by Cohen and Purcell (1967). Microliter quantities of 30 percent H_2O_2 solution are injected into a metered stream of air that flows into a Teflon bag. The concentration of H_2O_2 in the bag is then determined by the iodometric method discussed below.

4.2.7.4.2 Calibration. By far the most common method for standardizing low concentrations of H_2O_2 is based on iodometry (Allen et al., 1952; Hochanadel, 1952; Cohen et al., 1967). Hydrogen peroxide liberates iodine from an iodide solution quite slowly, but in the presence of a molybdate catalyst the reaction is quite rapid. The iodine liberated may be determined by titration with standard thiosulfate at higher concentrations or by photometric measurement of the tri-iodide ion at low concentrations. The molar absorption coefficient of the tri-iodide ion at 350 nm has been determined to be 2.44×10^4 by measuring 10^{-5} to 10^{-4} M H_2O_2 solutions prepared from 0.2 M stock H_2O_2 solution standardized against primary grade arsenious oxide (Armstrong and Humphreys, 1965). The stoichiometry is apparently 1 mole of iodine released per mole of H_2O_2. Definitive studies of the stoichiometry, however, have not been performed to the same extent as those of the stoichiometry for the iodometric determination of O_3.

4.3 SAMPLING, MEASUREMENT, AND CALIBRATION METHODS FOR PRECURSORS TO OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

During the last decade, a number of advances have been made in the methodology for determining nonmethane organic compounds and oxides of nitrogen. An overview of these advances is discussed in the following sections. In the case of measurement methods for nonmethane organic compounds (NMOCs), early ozone control models did not require speciation of the complex mixture of organics in ambient air. As a result, non-speciation methods were employed for the purpose of providing a data base for early photochemical modeling studies. As the air quality models grew more sophisticated, however, the need arose for more specific information concerning the organic composition of the atmosphere. Consequently, methodology was developed to provide for detailed speciation of NMOCs. In addition to improving the data base for photochemical modeling, the NMOC speciation techniques have also been utilized to characterize various sources of pollution (e.g., mobile versus stationary).

The development of methodology for oxides of nitrogen has likewise advanced since the original EPA Federal Reference Method for measurement of nitrogen dioxide, the Jacobs-Hochheiser technique, was withdrawn in 1973. A number of methods for nitric oxide and nitrogen dioxide have been proposed and evaluated since then and are described here.

4.3.1 Nonmethane Organic Compounds

Numerous sampling, analytical, and calibration methods have been employed to determine vapor-phase NMOCs in ambient air. Some of the analytical methods utilize detection techniques that are highly selective and sensitive to specific functional groups or atoms of a compound (e.g., formyl group of aldehydes, halogen), while others respond in a more universal manner; that is, to the number of carbon atoms present in the organic molecule. In this overview of the most pertinent measurement methods, NMOC have been arranged in three major classifications: nonmethane hydrocarbons, aldehydes, and other oxygenated compounds. Sampling, analytical, and calibration procedures are discussed for each classification. Reference is also made to those analytical methods utilized in more than one of the above classifications.

4.3.1.1 Nonmethane Hydrocarbons. Nonmethane hydrocarbons (NMHC) constitute the major portion of NMOC in ambient air (Chapter 3). Traditionally, NMHC have been measured by methods that employ a flame ionization detector (FID) as the sensing element. This detector was originally developed for gas chromatography and employs a sensitive electrometer that measures a change in ion intensity resulting from the combustion of air containing organic compounds. Ion formation is essentially proportional to the number of carbon atoms present in the organic molecule (Sevcik, 1975). Thus, aliphatic, aromatic, alkenic, and acetylenic compounds all respond similarly to give relative responses of 1.00 ± 0.10 for each carbon atom present in the molecule (e.g., 1 ppm hexane =

6 ppm C; 1 ppm benzene = 6 ppm C; 1 ppm propane = 3 ppm C). Carbon atoms bound to oxygen, nitrogen, or halogens give reduced relative responses (Dietz, 1967). Consequently, the FID, which is primarily used as a hydrocarbon measuring method, should more correctly be viewed as an organic carbon analyzer.

In the following sections, discussion focuses on the various methods utilizing this detector to measure total nonmethane organics. Methods in which no compound speciation is obtained are covered first. Methods for determining individual organic compounds are then discussed.

4.3.1.1.1 Non-speciation methods. The EPA reference method for nonmethane organic compounds, which was promulgated in 1971, involves the gas chromatographic separation of methane (CH_4) from the remaining organics in an air sample (F.R., 1971). A second sample is injected directly to the detector without methane separation. Subtraction of the first value from the second produces a nonmethane organic concentration.

A number of studies of commercial analyzers employing the Federal Reference Method have been reported (Reckner, 1974; McElroy and Thompson, 1975; Harrison et al., 1977; Sexton et al., 1982). In one of the first studies, analyses of known synthetic mixtures of hydrocarbons were conducted by 16 users of the reference method (Reckner, 1974). The nonmethane concentrations tested in this study were 0.23 and 2.90 ppm C. The results shown in Table 4-9 indicate the percentage error from the two known concentrations. At the 0.23 ppm level, the majority of the measurements were in error by amounts greater than 50 percent. At 2.90 ppm, most of the measurements were in error by only 20 percent or less.

In general, all of the above studies indicated an overall poor performance of the commercial instruments when either calibration or ambient mixtures containing NMOC concentrations less than 1 ppm C were used. The major problems associated with using these NMOC instruments have been reported in a recent technical assistance document (U.S. Environmental Protection Agency, 1981). The technical assistance document also suggests ways to reduce the effects of existing problems. Table 4-10 summarizes the major problem areas and lists recommendations for reducing these effects.

Other approaches to the measurement of nonmethane organics have also been investigated. One such method, developed in 1973, utilizes the fact that CH_4 requires more heat for combustion than other organics (Poli and Zinn, 1973). One portion of the air sample passes through a catalyst bed where all hydrocarbons except CH_4 are combusted. This sample stream then enters an FID where

TABLE 4-9. PERCENTAGE DIFFERENCE FROM KNOWN CONCENTRATIONS OF NONMETHANE HYDROCARBONS OBTAINED BY SIXTEEN USERS

Known concentration, ppm	% difference from given concentration				
	>100	50 to 100	20 to 50	10 to 20	0 to 10
0.23	6	4	3	2	1
2.90	2	0	3	2	9

Source: Reckner (1974).

the CH_4 concentration alone is recorded. The remaining portion of the sample passes directly to a second FID for a total organic carbon measurement. The simultaneous processing of both signals yields an NMOC value. Although it provides a continuous measurement of NMOC levels, this method is also subject to many of the same shortcomings attributed to the EPA reference method.

Recently, a prototype instrument that measures NMOCs by optical absorption has been developed (Manos et al., 1982). The unit oxidizes NMOCs to carbon dioxide (CO_2) and uses a non-dispersive infrared absorption technique to measure the organic burden indirectly. Ascarite serves to remove CO_2 initially present in air and a hopcalite catalyst selectively oxidizes organics other than methane to CO_2 and H_2O. Since carbon monoxide (CO) will also oxidize to CO_2 during this process, a dual-channel system is utilized to correct for the contribution from ambient CO concentrations. This unit performed well during a brief laboratory evaluation using calibration standards; however, more extensive laboratory and field tests are needed before the unit can be considered suitable for NMOC measurement.

Other methods under development and evaluation include oxidation-reduction schemes in which nonmethane organics are chromatographically separated from methane and non-organic species and then oxidized to CO_2, reduced to CH_4, and detected by FID (U.S. Environmental Protection Agency, 1978b). When organic carbon concentrations are greater than 100 ppb, the reduction step can be eliminated and a non-dispersive infrared analyzer can be used to detect the CO_2 formed during the oxidation step (Salo et al., 1975).

A method for measuring NMOC directly has been reported by Cox et al. (1982). This approach involves the cryogenic preconcentration of nonmethane organic compounds and the measurement of the revolatilized NMOCs using flame

TABLE 4-10. PROBLEMS ASSOCIATED WITH GATHERING NMOC DATA WITH AUTOMATED ANALYZERS AND RECOMMENDATIONS FOR REDUCING THESE EFFECTS

Problem Areas:

1. Contaminants may be present in compressed-gas cylinders containing calibration gases.
2. Compressed-gas cylinders of calibration gases sometimes contain the standard in a nitrogen or argon background. When no oxygen is blended with these gases, FID sensitivity is altered.
3. The assay of calibration gases contained in compressed-gas cylinders (as received from the supplier) is sometimes incorrect.
4. There are wide differences in the per-carbon response to different NMOC species.
5. FID analyzers require hydrogen, which presents a potential operational hazard.
6. The NMOC concentration is obtained by subtraction of two relatively large and nearly equal numbers ($TOC-CH_4=NMOC$) and thus is subject to large, relative errors.
7. NMOC analyzers may exhibit excessive zero and span drift during unattended operation.
8. The complex design of some NMOC analyzers creates unique problems that are generally not experienced in other pollutant analyzers. Meticulous set-up, calibration, and operation procedures (which are analyzer-specific) are difficult to understand and follow.

Recommendations:

1. Calibration gases should be checked to determine the concentration of contaminants.
2. Calibration concentrations should be obtained by dynamic dilution of a pollutant standard with zero-grade air containing oxygen. The dilution ratio should be sufficiently high (∿100:1) to ensure that the calibration sample contains 20.9% ± 0.3% oxygen.
3. All calibration standards contained in compressed-gas cylinders should be traceable to Standard Reference Materials from the National Bureau of Standards.
4. The NMOC response should be calibrated to a propane standard.
5. The operator should use documented procedures for hydrogen safety.
6. All channels should be properly calibrated.
7. The FIDs should be operated in accordance with instructions supplied by the manufacturer and this document.
8. The training of qualified operators should be augmented with a Technical Assistance Document, which provides detailed calibration and operation procedures for NMOC analyzers.

Source: U.S. Environmental Protection Agency (1981).

ionization detection. The procedure involves the following steps. A fixed volume of sample is drawn through a trap cooled to liquid argon temperature (liquid N_2 cannot be used since it will also condense methane and oxygen). At this temperature all NMOCs are condensed into the trap. After the residual CH_4 and oxygen are cleared from the trap by the helium carrier gas, the trap temperature is raised to revolatilize the NMOC. Oxygen removal reduces the variation in response to different organic compounds.

Jayanty et al. (1982) used a similar system to study the responses of a variety of aliphatic and aromatic compounds. Good linearity was observed with the cryogenic trapping procedure (500 ml of air) over a concentration range of 50 to 5,000 ppb C. Humidity did not generally interfere with the analysis. Sample precisions of ±5 percent for single- and multiple-component gas standards and ±10 percent for ambient samples were consistently achieved. Responses for aromatic compounds, however, were less than expected. The researchers recommended additional testing and instrument refinement in order to resolve this problem.

4.3.1.1.2 Speciation methods. The primary separation technique utilized for NMOC speciation is gas chromatography (GC). Coupled with flame ionization detection, this analytical method permits the separation and identification of many of the organic species present in ambient air.

Compound separation is accomplished by means of both packed and capillary GC columns. If high resolution is not required and large sample volumes are to be injected, packed columns are employed. The traditional packed column may contain either (1) a solid polymeric adsorbent (gas-solid chromatography) or (2) an inert support, coated with a liquid (gas-liquid chromatography). Packed columns containing an adsorbent substrate are required to separate C_2-C_3 compounds. The second type of column can be a support-coated or wall-coated open tubular capillary column. The latter column has been widely used for environmental analysis because of its superior resolution and broader applicability. The wall-coated capillary column consists of a liquid stationary phase coated or bonded (cross-linked) to the specially treated glass or fused-silica tubing. Fused-silica tubing is most commonly used because of its physical durability and flexibility. When a complex mixture is introduced into a GC column, the carrier gas (mobile phase) moves the sample through the packed or coated capillary column (stationary phase). The chromatographic process occurs as a result of repeated sorption-desorption of the sample components (solute) as they move along the stationary phase. Separation results from the different affinities that the solute components have for the stationary phase.

The GC-FID technique has been used by numerous researchers to obtain ambient NMOC data. Singh (1980) drew on the cumulative experience of these researchers to prepare a guidance document for state and local air pollution agencies interested in obtaining speciation data. In general, most researchers have employed two gas chromatographic units to carry out analyses of NMOC species in ambient air. The more volatile organic compounds (C_2 through C_5) are generally measured on one unit using packed-column technology, while the other GC separates the less volatile organics using a capillary column. In typical chromatograms of urban air, all major peaks are identified and, on a mass basis, represent from 65 to 90 percent of the measurable nonmethane organic burden. Identification of GC peaks is based upon matching retention times of unknown compounds with those of standard mixtures. The use of dedicated computer systems facilitates this task, but close scrutiny of the data is still necessary to correct periodic misidentification of unknown compounds resulting from variations in retention time. Subsequent verification of the individual species is normally accomplished with gas chromatographic/mass spectrometric (GC/MS) techniques. Compound-specific detection systems, such as electron capture, flame photometry, and spectroscopic techniques, have also been employed for peak identifications. A discussion of these systems, however, is beyond the scope of this report. Several documents covering these detection systems are available (Lamb et al., 1980; Riggin, 1983).

Because the organic components of the ambient atmosphere are present at ppb levels or lower, some means of sample preconcentration is necessary to provide sufficient material for the GC-FID system. The two primary techniques utilized for this purpose are the use of solid adsorbents and cryogenic collection. The more commonly used sorbent materials are divided into three categories: (1) organic polymeric adsorbents, (2) inorganic adsorbents, and (3) carbon adsorbents. Primary organic polymeric adsorbents used for NMOC analyses include the materials Tenax GC and XAD-2. These materials have a low retention of water vapor and, hence, large volumes of air can be collected. These materials do not, however, efficiently capture highly volatile compounds such as C_2 to C_5 hydrocarbons, nor certain polar compounds such as methanol and acetone. Primary inorganic adsorbents are silica gel, alumina, and molecular sieves. These materials are more polar than the organic polymeric adsorbents and are thus more efficient for the collection of the more volatile and polar compounds. Unfortunately, water is also efficiently collected, which in many instances leads to rapid deactivation of the adsorbent. Carbon adsorbents are less polar than the inorganic adsorbents and, as a result, water adsorption by carbon adsorbents is a less significant problem. The carbon-based materials also tend to exhibit much stronger adsorption properties than organic polymeric adsorbents; thus, lighter-molecular-weight species are more easily retained. These same adsorption effects result, however, in irreversible adsorption of many compounds. Furthermore, the very high thermal desorption temperatures required (350 to 400 °C) limit their use and also may lead to degradation of labile compounds. The commonly available classes of carbon adsorbents include: (1) various conventional activated carbons; (2) carbon molecular sieves (Spherocarb, Carbosphere, Carbosieve); and (3) carbonaceous polymeric adsorbents (Ambersorb XE-340, XE-347, XE-348).

Although a number of researchers have employed solid adsorbents for the characterization of selected organic species in air, only a few attempts have been made to identify and quantitate the range of organic compounds from C_2 and above. Westberg et al. (1980) evaluated several carbon and organic polymeric adsorbents and found that Tenax-GC exhibited good collection and recovery efficiencies for $\geq C_6$ organics; the remaining adsorbents tested (XAD-4, XE-340) were found unacceptable for the lighter organic fraction. The XAD-4 retained $\geq C_2$ organic gases, but it was impossible to completely desorb these species without partially decomposing the XAD-4. Good collection and recovery efficiencies were provided by XE-340 only for organics of C_4 and above.

Ogle et al. (1982) used a combination of adsorbents in series and designed an automated GC-FID system for analyzing C_2 through C_{10} hydrocarbons. Tenax GC was utilized for C_6 and above, while Carbosieve S trapped C_3 through C_5 organics. Silica gel followed these adsorbents and effectively removed water vapor while passing the C_2 hydrocarbons onto a molecular-sieve 5A adsorbent. The combined sorbents have been laboratory-tested with a 38-component hydrocarbon mixture. Good collection and recovery efficiencies were obtained. Preliminary field tests have also been successful, but a very limited data base exists. Futhermore, the current chromatographic procedures utilize packed-column technology. The addition of capillary columns to this system would permit better resolution of the complex mixtures typically found in ambient air.

The preferred method for obtaining NMOC data is cryogenic preconcentration (Singh, 1980). Sample preconcentration is accomplished by directing air through a packed trap immersed in either liquid oxygen (b.p. -183°C) or liquid argon (b.p. -186°C). For the detection of about 1 ppb C of an individual compound, a 250-cc air sample is normally processed. The collection trap is generally filled with deactivated 60/80 mesh glass beads (Westberg et al., 1974), although coated chromatographic supports have also been used (Lonneman et al., 1974). Both of the above cryogens are sufficiently warm to allow air to pass completely through the trap, yet cold enough to collect trace organics efficiently. This collection procedure also condenses water vapor. An air volume of 250 cc at 50 percent relative humidity and 25°C contains approximately 2.5 mg of water, which appears as ice in the collection trap. The collected ice at times will plug the trap and stop the sample flow; furthermore, water transferred to the capillary column during the thermal desorption step occasionally causes plugging and other deleterious column effects. To circumvent water condensation problems, McClenny et al. (1984) have employed a Nafion tube drier to remove water vapor selectively during the sample collection step. These researchers have constructed an automated cryogenic preconcentration sampling and analysis GC system using this drier and are currently conducting field evaluaton studies on their system.

In addition to direct sampling via preconcentration with sorbents and cryogenic techniques, collection of whole air samples is frequently used to obtain NMOC data. Rigid devices such as syringes, glass bulbs, or metal containers and non-rigid devices such as Tedlar and Teflon plastic bags are often utilized during sampling. The primary purpose of whole-air collection is to store an air sample temporarily until subsequent laboratory analysis is performed. The major problem with this approach is assuring the integrity of the sample contents prior to analysis. Of concern is whether sample components of interest are adsorbed or decomposed through interaction with the container walls or reaction with co-collected gases such as ozone and nitrogen dioxide. Sample condensation may also occur at elevated concentrations or when samples are stored under high pressures (i.e., in metal containers). Contamination from sampling containers is likewise a frequent occurrence (Lonneman et al., 1981; Seila et al., 1976). Table 4-11 summarizes the advantages and disadvantages of the primary collection media for NMOC analysis.

4.3.1.1.3 Calibration. Calibration procedures for NMOC instrumentation require the generation of dilute mixtures at concentrations expected to be

TABLE 4-11. SUMMARY OF ADVANTAGES AND DISADVANTAGES OF PRIMARY COLLECTION MEDIA FOR NMOC ANALYSIS

Sampling technique	Advantages	Disadvantages
1. Solid adsorbents	o Many sorbents do not retain H_2O vapor; thus, large volumes of air can be processed.	o No single adsorbent can be used to collect and recover organics of C_2 and above.
	o Integrated samples from a period of minutes to days are easily obtained.	o Contamination and artifact peaks plague many sorbent systems.
	o Sample cartridges are convenient for field use.	o Many adsorbents require high (>300°C) thermal desorption temperatures, which may lead to degradation of labile compounds, artifact peak formation, etc.
		o Breakthrough volume and collection and recovery efficiencies must be determined for each compound of interest.
2. Cryogenic preconcentration	o A wide range of organic material can be collected.	o Volume of air collected is limited by amount of moisture condensing.
	o Artifact problems are avoided.	o Liquid argon or oxygen is necessary for preconcentration.
	o Collected organics are immediately available for analysis, without solvent removal or use of high thermal desorption temperatures.	o Field collection apparatus is bulky compared to adsorbent cartridges.
	o Collected species are stable; good recovery efficiencies are obtained.	

TABLE 4-11 (continued). SUMMARY OF ADVANTAGES OF PRIMARY COLLECTION MEDIA FOR NMOC ANALYSIS

Sampling technique	Advantages	Disadvantages
3. Rigid containers (Metal canisters)	o Can be treated to make them chemically unreactive. o Durable; easy to clean, transport, and use. o Can be pressurized; leakage and permeation minimized. o Excellent stability for many trace species; long-term storage is possible.	o High initial cost. o Limited collection volume. o Difficult to collect integrated samples. o Sample may be lost to walls by condensation.
4. Non-rigid containers (Teflon and Tedlar Bags)	o Readily available. o Convenient for collecting integrated samples. o Good short-term stability of trace species.	o Subject to breakage (at seams) during handling. o Admits sunlight. o Slow permeation of chemicals out of and into plastic bags during storage. o Outgassing contamination from bag material. o Short storage life.

Source: Derived from Singh (1980); Jayanty et al. (1982); Sexton et al. (1982); National Research Council (1976); Lonneman et al. (1981); Holdren et al. (1982).

found in ambient air. Methods for generating such mixtures are classified as static or dynamic systems.

Static systems are generally preferred for quantitating NMOCs. The most commonly used static system is a compressed gas cylinder containing the appropriate concentration of the compound of interest. These cylinder gases may also be diluted with hydrocarbon-free air to provide multi-point calibrations. Calibration and hydrocarbon-free air cylinders are available commercially. Additionally, some standard gases such as propane and benzene are available from the National Bureau of Standards (NBS) as certified standard reference materials (SRM). Commercial mixtures are generally referenced against these NBS standards. In its recent technical assistance document for operating and calibrating continuous NMOC analyzers, the U.S. Environmental Protection Agency (1981) recommended propane-in-air standards for calibration. Some commercially available propane cylinders have been found to contain other hydrocarbons (Cox et al., 1982), so that all calibration data should be referenced to NBS standards. Because of the uniform carbon response of a GC-FID system (±10 percent) to hydrocarbons (Dietz, 1967), a common response factor is assigned to both identified and unknown compounds obtained from the speciation systems. If these compounds are oxygenated species, an underestimation of the actual concentrations will be reported. Dynamic calibration systems are employed when better accuracy is needed for these oxygenated hydrocarbon species. Dynamic systems are normally employed to generate *in situ* concentrations of the individual compound of concern and include devices such as permeation and diffusion tubes and syringe delivery systems.

4.3.1.1.4 *Comparison of non-speciation versus speciation methods*. Speciation methods involving cryogenic preconcentration have been compared with non-speciation NMOC analyzers in the following studies.

Jayanty et al. (1982) conducted a laboratory comparison between the prototype non-speciation method described earlier (Section 4.3.1.1.1) and their gas chromatographic separation method. Comparison of the two methods for 12 ambient air samples collected in stainless steel canisters showed agreement within ±15 percent. Ambient air concentrations ranged from 100 to 1000 ppb C.

Lonneman (1979) compared total NMOC and speciation methods during field studies in Houston in 1978. Samples were collected during 3-hour integrated time periods (6 to 9 a.m., 1 to 4 p.m.) in Tedlar bags for subsequent analysis. The correlation coefficients for 150 measurement pairs from five sites averaged 0.74. For data pairs of 500 ppb C and less, an average correlation coefficient

(r) of 0.55 was calculated, with a low value of 0.12 at one site. Lonneman attributed the low correlations to maintenance and calibration problems in the continuous analyzers and concluded that the results from the non-speciation method are "at best marginal for use in photochemical model applications."

Holdren et al. (1982) made a similar comparison during a 2-month study at urban sites in Cincinnati and Cleveland, Ohio. They utilized a GC/cryogenic trapping technique and compared their results with data from state-operated NMOC analyzers (SAROAD data). Ambient air samples were collected in Teflon bags (6 to 9 a.m. integrated collection) and were transferred immediately to pretreated aluminum cylinders for shipment and analysis at the central laboratory. Concentrations of NMOC ranged from 200 to 2100 ppb C. Linear regression analyses of the non-speciated versus speciated data resulted in correlation coefficients that ranged from 0.75 to 0.92 for the four urban sites (total of 67 comparisons). Limiting the comparisons to concentrations of 500 ppb C and lower resulted in an average correlation coefficient of 0.10.

Richter (1983) compared continuous total NMOC with GC speciation results obtained at seven fixed ground-level sites used in the Northeast Corridor Regional Modeling Project (NECRMP). The NMOC data were obtained in real time, while Teflon bags were used to collected integrated samples (6 to 9 a.m.) for the GC/cryogenic analyses. Over 60 comparisons were available from each site. Table 4-12 summarizes statistical information obtained from least-squares analysis of the data (Richter, 1983). As the table indicates, only data from the East Boston site exhibited a high correlation coefficient. This study represents the most extensive effort made yet to compare the two NMOC measuring methods. Emphasis was placed on correct instrument operation, calibration, etc.; and only verified data were compared. Yet the above results indicate that much more work is needed to resolve the differences between the two methods.

4.3.1.2 Aldehydes. Historically, the major problem in measuring concentrations of aldehydes in ambient air has been to find an appropriate monitoring technique that is sensitive to low concentrations and specific for the various homologues. Early techniques for measuring formaldehyde, the most abundant aldehyde, were subject to many interferences and lacked sensitivity at low ppb concentrations. The more recently developed techniques can be utilized to accurately measure the various types and amounts of aldehydes at ppb levels. This section describes those methods currently used for measuring aldehydes in ambient air.

TABLE 4-12. GC/CONTINUOUS NMOC ANALYZER COMPARISONS, LEAST-SQUARES REGRESSIONS

Location	Slope	Intercept, ppm C	Standard error	r^2
West End Library, Washington, DC	0.552	-0.552	0.672	0.169
Read Street, Baltimore, MD	0.113	-0.283	0.713	0.0077
Essex, MD	0.835	-0.101	0.599	0.354
Linden, NJ	0.531	NA[a]	0.865	0.141
Newark, NJ	0.987	-0.277	0.574	0.467
East Boston, MA	1.108	+0.095	0.327	0.887
Watertown, MA	0.750	-0.568	0.574	0.475

[a] Data not available.

Source: Richter (1983).

These include the chromotropic acid (CA) method for formaldehyde, the 3-methyl-2-benzothiazolone hydrazone (MBTH) technique for total aldehydes, Fourier-transform infrared (FTIR) spectroscopy, and the high-performance liquid chromatography (HPLC) method employing 2,4-dinitrophenylhydrazine (DNPH) derivatization.

4.3.1.2.1 Chromotropic acid method. The chromotropic acid method (CA) involves the collection of formaldehyde in a midget impinger containing an aqueous mixture of chromotropic and sulfuric acids, followed by the spectrophotometric measurement of absorbance of the resulting color (Altshuller and McPherson, 1963; U.S. Dept. of Health, Education and Welfare, 1965). A modification described by Johnson et al. (1981) improved the accuracy and sensitivity of the CA method by reducing the concentration of sulfuric acid and by eliminating a heating cycle, relying solely on the heat of solution generated by sulfuric acid (Altshuller et al., 1961; Olansky and Deming, 1976). Trapping formaldehyde in a 1 percent bisulfite solution before adding the CA solution increased collection efficiency from 84 percent to 92 percent with no sulfite interferences.

The CA method for measuring formaldehyde has been widely studied (Salas and Singh, 1982; Grosjean and Kok, 1981; National Research Council, 1981; Tuazon et al., 1980; Lloyd, 1979). Originally developed as a spot-test by Eegriwe (1937), it was adopted to quantitate formaldehyde spectrophotometrically (Bricker and Johnson, 1945; West and Sen, 1956) and was modified for ambient air measurements in the early 1960s (Altshuller et al., 1961; Altshuller and McPherson, 1963; U.S. Dept. of Health, Education, and Welfare, 1965). While used widely today for both occupational and ambient air environments, its specificity for formaldehyde, which accounts for approximately half of total ambient air aldehydes (see Section 3.5), limits its usefulness for characterizing aldehyde concentrations in ambient air.

The CA method has been reported to be sensitive to acrolein, acetaldehyde, phenol, nitrogen dioxide, and nitrates (National Research Council, 1981; Krug and Hirt, 1977; U.S. Dept. of Health, Education, and Welfare, 1973; Sleva, 1965; Altshuller et al., 1961). Recent work, however, indicates that neither nitrates, nitrites, NO_2, nor acetaldehyde at elevated ambient air levels interfere with the CA analysis (Johnson et al., 1981; Grosjean and Kok, 1981). Relevant data on other interfering agents were not found.

4.3.1.2.2 MBTH method. A spectrophotometric technique for total aldehydes was developed in the early 1960s by Sawicki et al. (1961). Known as the MBTH method, it involves the reaction of aldehyde with 3-methyl-2-benzothiazolone hydrazone to form an azine that is oxidized by a ferric chloric-sulfamic acid solution to form a blue cationic dye (Altshuller, 1983; U.S. Dept. of Health, Education, and Welfare, 1965; Hauser and Cummins, 1964; Altshuller and McPherson, 1963; Altshuller and Leng, 1963; Altshuller et al., 1961).

The MBTH method has a reported sensitivity of 15 ppb for, primarily, low-molecular-weight aldehydes (National Research Council, 1981). The method is subject to interferences by NO_2 and gives an inconsistent response to higher-molecular-weight aldehydes (Sawicki et al., 1961; Altshuller et al., 1961). Nonetheless, the Intersociety Committee of the American Public Health Association recommends the MBTH colorimetric method for determining total aldehydes in air (Intersociety Committee, 1977a). Miksch and Anthon (1982) devised a sampling and analysis scheme that permits a single MBTH sample to be used for both formaldehyde and total aliphatic aldehyde determinations.

4.3.1.2.3 Fourier-transform infrared spectroscopy. Infrared absorption spectroscopy has been used to identify and measure aldehydes in ambient air (Hanst et al., 1975, 1982; Tuazon et al., 1978, 1980, 1981a). These studies employ Fourier-transform infrared (FTIR) spectrometers interfaced to multiple reflection cells operating at total optical paths of up to 1 km. At such pathlengths, a detection limit of a few ppb is achieved for formaldehyde. The advantages of the long-pathlength FTIR method for ambient air aldehyde measurements (i.e., good specificity and direct in situ analysis) are offset by the relatively high cost and lack of portability of such systems.

4.3.1.2.4 High-performance liquid chromatography (HPLC) 2,4-dinitrophenylhydrazine (DNPH) method. This method takes advantage of the reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazone:

$$RR'C{=}O + NH_2NHC_6H_3(NO_2)_2 \longrightarrow H_2O + RR'C{=}NNHC_6H_3(NO_2)_2 \quad (4\text{-}17)$$

Since DNPH is a weak nucleophile, the reaction is carried out in the presence of acid in order to increase protonation of the carbonyl.

The HPLC-DNPH method is the preferred way of measuring aldehydes in ambient air. Atmospheric sampling is usually conducted with micro-impingers containing an organic solvent and aqueous, acidified DNPH reagent (Papa and Turner, 1972; Katz, 1976; Smith and Drummond, 1979; Fung and Grosjean, 1981). After sampling is completed, the hydrazone derivatives are extracted and the extract is washed with deionized water to remove the remaining acid and unreacted DNPH reagent. The organic layer is then evaporated to dryness, subsequently dissolved in a small volume of solvent, and analyzed by reversed-phase liquid chromatographic techniques employing an ultraviolet (UV) detection system. Analysis by a flame ionization detection (FID) system has proved less successful than UV because the derivatives are not really amenable to GC-FID analysis.

An improved procedure has been reported that is much simpler than the above aqueous impinger method (Lipari and Swarin, 1982; Kuntz et al., 1980; Tanner and Meng, 1984). This scheme utilizes a midget impinger containing an acetonitrile solution of DNPH and an acid catalyst. After sampling, an aliquot of the original collection solution is directly injected into the liquid chromatograph. This approach eliminates the extraction step and several sample-handling procedures associated with the DNPH-aqueous solution; and provides much better recovery efficiencies. Lipari and Swarin (1982) have reported detection limits of 20, 10, 5, and 4 ppb for formaldehyde, acetaldehyde, acrolein, and benzaldehyde, respectively, in 20-liter air samples. These researchers have also developed a newer technique employing a solid adsorbent cartridge containing Florisil coated with 2,4-dinitrophenyldrazine (Lipari and Swarin, 1985). Collection efficiencies greater than 90 percent were obtained at low ppb levels. A detection limit of 1 ppb of HCHO for a 100-liter air sample was achieved.

4.3.1.2.5 Calibration of aldehyde measurements. Since they are reactive compounds, it is extremely difficult to make stable calibration mixtures of aldehydes in pressurized gas cylinders. Although gas-phase aldehyde standards are available commercially, the vendors do not guarantee any level of accuracy.

Formaldehyde standards are generally prepared by one of several methods. The first method utilizes dilute commercial formalin (37 percent formaldehyde, w/w). Calibration is accomplished by the direct spiking into sampling impingers of the diluted mixture or by evaporation into known test volumes, followed by impinger collection. Formaldehyde can also be prepared by heating known amounts of paraformaldehyde, passing the effluent gases through a methanol-liquid nitrogen slush trap to remove impurities, and collecting the remaining formaldehyde. Paraformaldehyde permeation tubes have also been used (Tanner and Meng, 1984).

For the higher-molecular-weight aldehydes, liquid solutions can be evaporated or pure aldehyde vapor can be generated in dynamic gas-flow systems (permeation tubes, diffusion tubes, syringe delivery systems, etc.). These test atmospheres are then passed through the appropriate aldehyde collection system and analyzed. A comparison of these data, with the direct spiking of liquid aldehydes into the particular collection system, provides a measure of the overall collection efficiency.

4.3.1.2.6 Comparison of measurement methods. Several side-by-side comparisons of the chromotropic acid method (CA) with other methods have been reported. Grosjean and Kok (1981) compared the CA method (Johnson et al., 1981) with HPLC-DNPH (Fung and Grosjean, 1981) and FTIR spectroscopy (Tuazon et al., 1978). They found fairly close agreement between the CA and HPLC-DNPH methods, but noted consistently higher results with FTIR. Corse (1981) sampled ambient air with CA (U.S. Dept. of Health, Education, and Welfare, 1965), MBTH (U.S. Dept. of Health, Education, and Welfare, 1965), and HPLC-DNPH methods (Kuntz et al., 1980). An examination of tabulated data from the Corse study shows a consistent and considerable difference between CA and HPLC measurements. For 25 CA measurements, formaldehyde averaged 8.8 ppb; while HPLC measurements from the same sampling train averaged 14.2 ppb. Overall, formaldehyde levels were approximately 60 percent higher with HPLC than with CA measurements.

Because blanks were not utilized for the HPLC analyses, however, the HPLC data are subject to uncertainty, since blank corrections can affect results substantially (Altshuller, 1983a). During laboratory studies, Kuntz et al. (1980) reported reasonable agreement (±7 percent) among the HPLC-DNPH, CA, FTIR, and GC-FID methods when low ppb levels of formaldehyde, acetaldehyde, propionaldehyde, hexanal, and benzaldehyde were generated.

4.3.1.3 Other Oxygenated Organic Species. As mentioned earlier, unsubstituted hydrocarbons constitute the major fraction of vapor-phase organic compounds occurring in ambient air. Aldehydes as a class of volatile organics appear second in abundance. With the exception of formic acid (Hanst et al., 1982; Tuazon et al., 1981a, 1980, 1978), other oxygenated species are seldom reported. The lack of data for oxygenated hydrocarbons is somewhat surprising since significant quantities of these species are emitted directly into the atmosphere by solvent-related industries (methanol, ethanol, acetone, etc.; see Chapter 3). Along with manmade emissions, natural sources of oxygenated hydrocarbons also contribute to this total. In addition to these direct emissions, it is also expected that photochemical reactions of hydrocarbons with oxides of nitrogen, ozone, and hydroxyl radicals will produce significant quantities of oxygenated products.

Difficulties in sample collection and analysis may account for this lack of data. The adsorptive nature of the surfaces that contact these oxygenated species often complicates the process of compound quantitation. The approach used for analysis of oxygenated and other polar organic compounds is to decrease adsorption by deactivating the interior surfaces of analytical hardware. A novel method has been reported, however, in which the reactive compounds of interest are modified rather than the surfaces with which these compounds interact (Osman et al., 1979; Westberg et al., 1980). In these studies, the laboratory derivatization of vapor-phase alcohols and acids (silylation) was investigated to evaluate the potential of such a procedure for stabilizing these polar compounds prior to analysis. Results indicate that silylation procedures greatly reduce adsorption of alcohols and acids and that, qualitatively, the silylated derivatives can be detected via the GC-FID system.

4.3.2 Nitrogen Oxides

In highly polluted urban air, the two most abundant oxides of nitrogen compounds are nitric oxide (NO) and nitrogen dioxide (NO_2). Both compounds, together designated as NO_x, participate in the photooxidation reactions in the atmosphere that lead to the formation of ozone (Chapter 3). Other minor reactive oxides of nitrogen in ambient air include peroxyacyl nitrates, nitrogen trioxide, dinitrogen pentoxide, and peroxynitric acid. In rural areas, and in urban areas late in the day and at night, these species may constitute a significant fraction of the total oxides of nitrogen in ambient air (Singh and Hanst, 1981; Killus and Whitten, 1985).

Analytical methods for NO_2 and NO are briefly described in this section. Older methods, including the former Federal Reference Method (Jacobs-Hochheiser method), are described in the criteria document on nitrogen oxides prepared by the U.S. Environmental Protection Agency (1982).

4.3.2.1 Measurement Methods for NO_2 and NO. In 1976, the continuous chemiluminescence method was promulgated as the new Federal Reference Method (F.R., 1976c). This method measures atmospheric concentrations of NO_2 indirectly by first reducing or thermally decomposing the gas quantitatively to NO (with a converter), reacting NO with O_3, and measuring the light intensity from the chemiluminescent reaction (Fontijn et al., 1970). Two types of converters have been employed for converting NO_2 to NO. In carbon or ferrous sulfate converters, NO_2 is chemically reduced to NO with the concurrent oxidation of converter material. Thermal converters, such as stainless or molybdenum steel converters, spontaneously decompose NO_2 to NO at elevated temperatures. The type and severity of interfering species will depend upon the converter used and the temperature of operation. The NO in the air stream is measured separately and subtracted from the previous NO_x (NO plus NO_2) measurement to yield the NO_2 concentration. Typical commercial chemiluminescence instruments can detect levels as low as 2.5 $\mu g/m^3$ (0.002 ppm) (Katz, 1976).

While all oxides of nitrogen and organic nitrogen compounds are thermodynamically unstable with respect to the formation of NO, the rate of the conversion to NO is infinitesmally slow under normal conditions. In the presence of reducing agents or at elevated temperatures, however, the conversion may become quite rapid. A number of studies have shown for example, that some species found in ambient air can undergo reduction by converters, resulting in positive interferences. Winer et al. (1974), for example, found that peroxyacetyl nitrate (PAN) and various nitrogen compounds are reduced by the converter to NO and that nitroethane and nitric acid are partially reduced in the system when a carbon (reducing) converter or a molybdenum (thermal decomposition) converter is used. Joshi and Bufalini (1978) reported positive interferences from halocarbons when a heated carbon converter was used; they also suggested that stainless steel converters may be subject to interferences from chlorinated hydrocarbons. Other evidence suggests that ammonia (NH_3) may be converted to NO in high-temperature thermal converters (U.S. Environmental Protection Agency, 1982). Positive interferences resulting from the presence of PAN and HNO_3 on afternoons of high oxidant concentrations can exceed 30 percent of the NO_2 concentrations (Spicer et al., 1979). Grosjean (1982) also reported that positive interferences from nitric acid and PAN during NO_2 analysis by chemiluminescence can cause a 50 to 60 percent NO_2 overestimation during smog conditions in Los Angeles. In less severe smog, the overestimation should not be this high.

Other acceptable methods for measuring ambient NO_2 levels, including two methods designated as equivalent methods, are the Lyshkow-modified Griess-Saltzman method, the instrumental colorimetric Griess-Saltzman method, the triethanolamine method, the sodium arsenite method, and the TGS-ANSA method [TGS-ANSA = triethanolamine, guaiacol (o-methoxyphenol), sodium metabisulfite, and 8-anilino-1-naphthalene sulfonic acid]. The sodium arsenite method and the TGS-ANSA method were designated as equivalent methods in 1977. While some of these methods measure the species of interest directly, others require oxidation, reduction, or thermal decomposition of the sample, or separation from interferences, before measurement. These methods have been described in the 1982 criteria document on nitrogen oxides (U.S. Environmental Protection Agency, 1982).

In addition to the wet chemical methods for measuring NO_2, other techniques have been investigated. Maeda et al. (1980) have reported a new chemiluminescence method based on the reaction of NO_2 with luminol (5-amino-2,3-dihydro-1,4-phthalazine dione), with a detection limit of about 50 parts per trillion (ppt) and linearity over a range of 0.5 ppb to 100 ppm. Work is under way by Maeda and coworkers to remove the interferences of O_3 and SO_2. Wendel et al. (1983) have reported the development of a luminol-based instrument for the continuous measurement of NO_2 in ambient air. In the early instrument developed by Maeda et al. (1980), response time was slow and the luminol solution pool in the detector cell showed chemiluminescence long after NO_2 was removed. The Wendel et al. (1983) instrument has rapid response time and luminol contacts the air sample via a filter paper strip rather than a pool of liquid. The method has a detection limit of 30 parts per trillion and has been freed of O_3 interference through modifications to the inlet system and the addition of

Na_2SO_3 to the luminol solution. Other workers have endeavored to improve chemiluminescence analyzers through physical modifications (e.g., Ridley and Howlett, 1974; Schiff et al., 1979).

Lipari (1984) has developed a solid-sorbent method for measuring NO_2 in ambient air. The NO_2 is quantitatively collected by means of a commericially available air sampling cartridge containing Florisil (magnesium silicate) coated with diphenylamine (DPA). The NO_2 reacts with DPA to form 2-nitro-4-nitro-, and N-nitroso-DPA derivatives. The products are eluted from the cartridge with methanol, acidified with a 1 N HCl catalyst to ensure recovery of the DPA derivatives, and analyzed by HPLC-UV. No interferences from NO, O_3, HNO_3, SO_2 and humidity were found, but PAN was found to produce a 50% positive interference. Storage stability tests indicated that cartridge blanks are stable for at least 3 months and that samples can be transported, stored, and analyzed for at least a period of 4 weeks after collection without significant sample loss or degradation. The reported limit of detection is 0.1 ppb NO_2 for a 2000-liter air sample, which corresponds to an 8-hr sampling period at a flow rate of 4 liters/min.

Molecular correlation spectrometry, in which an absorption band of a sample is compared with a corresponding band stored in the spectrometer, has been applied in analysis of NO_2 (Williams and Kolitz, 1968). Instruments processing the second derivative of sample transmissivity have also been used (Hagar and Anderson, 1970), as have infrared lasers and infrared spectrometers (Hanst, 1970; Hinkley and Kelley, 1971; and Kreuzer and Patel, 1971). Tucker et al. (1973, 1975) reported on instruments based on the principle of laser-induced fluorescence at optical frequencies. Fincher et al. (1977) described detection of 1 ppb NO_2 with a technique based on fluorescence by a pulsed xenon flashlamp. Long-pathlength differential optical absorption spectroscopy has also been employed to monitor NO_2 in the troposphere (Platt et al., 1980, 1984).

The preferred approach for measuring NO is also the continuous chemiluminescence method. Other methods for measuring NO directly include ferrous sulfate absorption and spectrophotometric measurement of the resulting ion (Norwitz, 1966), ultraviolet spectroscopy (Sweeny et al., 1964), infrared spectroscopy (Lord et al., 1975), and ultraviolet fluorescence (Okabe and Schwartz, 1975). Mass spectrometry and gas chromatography may also be employed.

4.3.2.2 Sampling Requirements. When sampling for NO_x, long residence times in sampling lines should be avoided. In the ambient air, the rate of photolysis of NO_2 (forming NO and O, and thus O_3) is almost equal to the rate of the reaction of the NO and O_3 to form NO_2. In sampling lines, photolysis stops but NO continues to react with O_3, producing NO_2. The magnitude of the dark reaction of NO with O_3 depends, of course, on the concentrations of NO and O_3 in the sample being analyzed, as well as on the residence time of the sample in the line. This dark reaction has practical consequences only under certain conditions. In moderately polluted urban areas, steady-state concentrations of NO are almost certainly too low at the period of maximal O_3 to cause significant errors in obtaining NO_x or O_3 measurements. Conversely, when O_3 is at a minimum, as in the early morning or possibly even in the late afternoon, NO (and NO_2) may be at maximal levels, and no significant errors would be introduced. If the concentrations of NO and O_3 are both low as in some rural areas, or during those brief periods in polluted areas when NO and O_3 diurnal patterns cross, then measurement errors could be introduced. Such errors are not likely to be significant, however.

Techniques for limiting sampling errors sampling to given levels of tolerance are reviewed by Butcher and Ruff (1971). In general, only glass or Teflon materials should be used in sampling trains. Among absorbents, granules impregnated with triethanolamine are reported to be the best, converting only 2 to 4 percent of the incoming NO_2 to NO (Intersociety Committee, 1977b; Huygen, 1970). The most frequently used oxidizer is chromic oxide on a firebrick granule support (Intersociety Committee, 1977b; Levaggi et al., 1974).

4.3.2.3 Calibration. Calibration procedures for NO_x measurements methods are critical for obtaining accurate analyses. Measurement methods for NO and NO_2 are calibrated (1) by sampling a gas stream of known concentration prepared from standard reference materials (SRMs); and (2) in the case of chemiluminescence analyzers, by determining converter efficiency. The SRM for NO is a cylinder of compressed NO in N_2 (50 and 100 ppm). The initial accuracy and the stability with time of this mixture were found to be quite good in a study conducted at the National Bureau of Standards (Hughes, 1975). An accuracy of 1 percent of the labeled concentrations was obtained as determined from pressure or gravimetric measurements. Concentration changes of less than 1 percent were observed over a 7-month period. The SRM for NO_2 is the NO_2 permeation tube (O'Keeffe and Ortman, 1966; Scaringelli et al., 1970). These tubes are calibrated by determining the permeation rate by means of weight-loss measurements at a constant temperature; or, in some cases, by means of micromanometric measurements. Both the NO and NO_2 SRMs are commercially available from sources traceable to SRMs maintained at the National Bureau of Standards.

Procedures for preparing calibrated gas streams call for an accurately measured dilution of the output of the NO and NO_2 SRMs. Likewise, the flow from the NO-in-N_2 cylinder must be accurately measured, as well as the diluent air flow. The flow of diluent air over the NO_2 permeation tube, maintained at constant temperature, must also be accurately measured. An alternative procedure commonly employed for the calibration of NO, NO_2, and NO_x measurements is the use of gas-phase titration (Rehme et al., 1974). A constant flow of O_3 is added to a diluted gas stream of NO at a higher concentration and the reaction mixture is monitored with an NO monitor, e.g., chemiluminescence. Because of the straightforward bimolecular reaction,

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4\text{-}18)$$

the NO consumed is equivalent to the O_3 added and the NO_2 produced. Thus, if the concentration of one of the constituents is known, the concentrations of the other two are readily determined. The U.S. Environmental Protection Agency (1976a,b) recommends the combined use of permeation tubes and gas-phase titration, using one technique to check the other.

To help ensure the quality of aerometric and NO_x exposure data, the U.S. Environmental Protection Agency issued a technical assistance document for NO_x measurement and calibration methods. The information summarized above is presented in detail in that document (U.S. Environmental Protection Agency, 1975).

4.4 SUMMARY

4.4.1 Sampling and Measurement of Ozone and Other Photochemical Oxidants

The analysis of ozone and other, related atmospheric oxidants includes requirements for representative sampling, specific and sensitive measurement methodologies, methods for the generation of standard samples, absolute methods for the calibration of these standards, and procedures by which to provide quality assurance for the whole measurement process. In this summary, recommended procedures are given for all of these analytical steps. Because of the large existing data base that employed measurements for "total oxidants," non-specific iodometric techniques are discussed and compared to current specific O_3 measurements.

4.4.1.1 Quality Assurance and Sampling. A quality assurance program is employed by the U.S. Environmental Protection Agency for assessing the accuracy and precision of monitoring data and for maintaining and improving the quality of ambient air data. Procedures and operational details have been prescribed in each of the following areas: selection of analytical methods and instrumentation (i.e., reference and equivalent methods); method specifications for gaseous standards; methods for primary and secondary (transfer standards) calibration; instrumental zero and span check requirements, including frequency of checks, multiple-point calibration procedures, and preventive and remedial maintenance requirements; procedures for air pollution episode monitoring; methods for recording and validating data; and information on documenting quality control (U.S. Environmental Protection Agency, 1977b). Design criteria for O_3 monitoring stations, to help ensure the quality of aerometric data, have been established (U.S. Environmental Protection Agency, 1977a; National Research Council, 1977).

4.4.1.2 Measurement Methods for Total Oxidants and Ozone. Techniques for the continuous monitoring of total oxidants and O_3 in ambient air are summarized in Table 4-13. The earliest methods used for routinely monitoring oxidants in the atmosphere were based on iodometry. When atmospheric oxidants are absorbed in potassium iodide (KI) reagent, the iodine produced,

$$O_3 + 3I^- + H_2O \rightarrow I_3^- + O_2 + 2OH^- \qquad (4\text{-}18)$$

is measured by ultraviolet absorption in colorimetric instruments and by amperometric means in electrochemical instruments. The term "total oxidants" is of historical significance only and should not be construed to mean that such measurements yield a sum of the concentrations of the oxidants in the atmosphere. The various oxidants in the atmosphere react to yield iodine at different rates and with different stoichiometries. Only ozone reacts immediately to give a quantitative yield of iodine. As discussed below, the total oxidants measurement correlates fairly well with the specific measurement of ozone, except during periods when significant nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) interferences are present. The major problem with the total oxidants measurement was the effect of these interferences. Total

TABLE 4-13. SUMMARY OF OZONE MONITORING TECHNIQUES

Principle	Reagent	Response	Minimum detection limit	Response time, 90% FS[a]	Major interferences	References
Continuous colorimetric	10(20)% KI buffered at pH = 6.8	Total oxidants	0.010 ppm	3 to 5 minutes	NO_2(+20%, 10%KI) SO_2(-100%)	Littman and Benoliel (1953) Tokiwa et al. (1972)
Continuous electrochemical	2% KI buffered at pH = 6.8	Total oxidants	0.010 ppm	1 minute	NO_2(+6%) SO_2(-100%)	Brewer and Milford (1960) Mast and Saunders (1962) Tokiwa et al. (1972)
Chemiluminescence	Ethylene, gas-phase	O_3-specific	0.005 ppm	< 30 seconds	None[b]	Nederbragt et al. (1965) Stevens and Hodgeson (1973)
Chemiluminescence	Rhodamine-B	O_3-specific	0.001 ppm	< 1 minute	None	Regener (1960, 1964) Hodgeson et al. (1970)
Ultraviolet photometry	None	O_3-specific	0.005 ppm	30 seconds	Species that absorb at 254 nm[c]	Bowman and Horak (1972)

[a] FS = full response.

[b] A signal enhancement of 3 to 12% has been reported for measurement of O_3 in humid versus dry air (California Air Resources Board, 1976).

[c] No significant interferences have been reported in routine ambient air monitoring. If abnormally high concentrations of species that absorb at 254 nm (e.g., aromatic hydrocarbons and mercury vapor) are present, some positive response may be expected. If high aerosol concentrations are sampled, inlet filters must be used to avoid a positive response.

oxidants instruments have now been replaced by specific ozone monitors in all aerometric networks and in most research laboratories. Biases among and between total oxidants and ozone methods are still important, however, for evaluating existing data on health and welfare effects levels where concentrations were measured by total oxidants methods.

The reference method promulgated by EPA for compliance monitoring for ozone is the chemiluminescence technique based on the gas-phase ozone-ethylene reaction (F.R., 1971). The technique is specific for ozone, the response is a linear function of concentration, detection limits of 0.001 to 0.005 ppm are readily obtained, and response times are 30 seconds or less. Prescribed methods of testing and prescribed performance specifications that a commercial analyzer must meet in order to be designated as a reference method or an equivalent method have been published by EPA (F.R., 1975b). An analyzer may be designated as a reference method if it is based on the same principle as the reference method and meets performance specifications. An acceptable equivalent method must meet the prescribed performance specifications and also show a consistent relation with the reference method.

The designated equivalent methods are based on either the gas-solid chemiluminescence procedure or the ultraviolet absorption procedure (Table 4-13). The first designated equivalent method was based on ultraviolet absorption by ozone of the mercury 254 nm emission line. The measurement is in principle an absolute one, in that the ozone concentration can be computed from the measured transmission signal since the absorption coefficient and pathlength are accurately known. In the gas-solid chemiluminescence analyzer, the reaction between ozone and Rhodamine-B adsorbed on activated silica produces chemiluminescence, the intensity of which is directly proportional to ozone concentration.

4.4.1.3 Calibration Methods. All the analyzers discussed above must be calibrated periodically with ozonized air streams, in which the ozone concentration has been determined by some absolute technique. This includes the ultraviolet (UV) absorption analyzer, which, when used for continuous ambient monitoring, may experience ozone losses in the inlet system because of contamination.

A primary ozone calibration system consists of a clean air source, ozone generator, sampling manifold, and means for measuring absolute ozone concentration. The ozone generator most often used is a photolytic source employing a mercury lamp that irradiates a quartz tube through which clean air flows at a controlled rate (Hodgeson et al., 1972). Once the output of the generator has been calibrated by a primary reference method, it may be used to calibrate O_3 transfer standards, which are portable generators, instruments, or other devices used to calibrate analyzers in the field. Reference calibration procedures that have been used for total oxidants and ozone-specific analyzers in the United States are summarized in Table 4-14.

The original reference calibration procedure promulgated by EPA was the 1 percent neutral buffered potassium iodide (NBKI) method (F.R., 1971). This technique was employed in most of the United States, with the exception of California. The California Air Resources Board (CARB) (1976) and the Los Angeles Air Pollution Control District (LAAPCD) employed different versions of iodometric techniques. Procedural details of the calibration methods are summarized in Table 4-14. A number of studies conducted between 1974 and 1978 revealed several deficiencies with KI methods, the most notable of which were poor precision or interlaboratory comparability and a positive bias of NBKI measurements relative to simultaneous absolute UV absorption measurements. The positive bias observed is peculiar to the use of phosphate buffer in the NBKI techniques. The bias was not observed in the unbuffered LAAPCD method (which nevertheless suffered from poor precision), nor in the 1 percent EPA KI method without phosphate buffer (Hodgeson et al., 1977), nor in a KI procedure that used boric acid as buffer (Flamm, 1977). A summary of results of these prior studies was presented in the previous criteria document (U.S. Environmental Protection Agency, 1978a) and in a review by Burton et al. (1976). Correction factors for converting NBKI calibration data to a UV photometry basis are given in Table 4-14 and discussed in Section 4.2.4.2.1.

Subsequently, EPA evaluated four alternative reference calibration procedures and selected UV photometry on the basis of superior accuracy and precision and simplicity of use (Rehme et al., 1981). In 1979 regulations were amended to specify UV photometry as the reference calibration procedure (F.R., 1979e). Laboratory photometers used as reference systems for absolute O_3 measurements have been described by DeMore and Patapoff (1976) and Bass et al. (1977).

These laboratory photometers contain long path cells (1 to 5 m) and employ sophisticated digital techniques for making effective double beam measurements of small absorbancies at low ozone concentrations. A primary standard UV photometer is one that meets the requirements and specifications given in the revised ozone calibration procedures (F.R., 1979e). Since these are currently available in only a few laboratories, EPA has allowed the use of

TABLE 4-14. OZONE CALIBRATION TECHNIQUES

Method	Reagent	Primary standard[a]	Organization and dates	Purpose	Bias, $[O_3]_i/[O_3]_{uv}$
1% NBKI	1% KI, phosphate buffer pH = 6.8	Reagent grade arsenious oxide	EPA 1971-1976	Primary reference procedure	1.12 ± 0.05[b]
2% NBKI[c]	2% KI phosphate buffer pH = 6.8	Reagent grade potassium biiodate	CARB until 1975	Primary reference procedure	1.20 ± 0.05[b]
1% Unbuffered KI	1% KI pH = 7		LAAPCD until 1975	Primary reference procedure	0.96[d]
UV photometry	None	O_3 absorptivity at Hg 254 nm emission line	All 1979-present	Primary reference procedure[e]	
Gas-phase titration (GPT)	Nitric oxide standard reference gas	Nitric oxide SRM (50 ppm in N_2) from NBS	EPA, States 1973-present	Alternative reference procedure (1973-1979) Transfer standard (1979-present)	1.030 ± 0.015[f]
1% BAKI	1% KI, boric acid buffer pH = 5	Standard KIO_3[g] solutions	EPA 1975-1979	Alternative reference procedure	1.00 ± 0.05

[a] In the case of the iodometric methods, the primary standard is the reagent used to prepare or standardize iodine solutions.

[b] The uncertainty limits represent the range of values obtained in several independent studies.

[c] Pre-humidified air used for the ozone source.

[d] Only one study available (DeMore et al., 1976).

[e] UV photometry used as reference method by CARB since 1975. This technique used as an interim, alternative reference procedure by EPA from 1976 to 1979.

[f] This is the value reported in the latest definitive study (Fried and Hodgeson, 1982). Previous studies reported biases ranging from 0 to 10 percent (Burton et al., 1976; Paur and McElroy, 1979).

[g] This procedure also recommended a standard I_3^- solution absorptivity to be used instead of the preparation of standard iodine solutions.

transfer standards, which are devices or methods that can be calibrated against a primary standard and transferred to another location for calibration of O_3 analyzers. Examples of transfer standards that have been used are commercial O_3 photometers, calibrated generators, and gas-phase titration (GPT) apparatus. Guidelines on transfer standards have been published by EPA (McElroy, 1979).

4.4.1.4 Relationships of Total Oxidants and Ozone Measurements. The temporal and quantitative relationship between simultaneous total oxidants and ozone measurements has been examined in this chapter because of the existence of a data base obtained by total oxidants measurements. Such a comparison is complicated by the relative scarcity of simultaneous data, the presence of both positive (NO_2) and negative (SO_2) interferences in total oxidants measurements of ambient air, and the change in the basis of calibration. In particular, the presence of NO_2 and SO_2 interferences prevent the establishment of a definite quantitative relationship between ozone and oxidants data. Nevertheless, some interesting conclusions can be drawn and are summarized below.

Studies concluded in the early to mid-1970s were reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1978a). Averaged data showed fairly good qualitative and quantitative agreement between diurnal variations of total oxidants and ozone. For example, uncorrected monthly averaged data from Los Angeles and St. Louis showed distinct morning and evening peaks resulting from NO_2 interference (Stevens et al., 1972a,b). The most recent comparison in the literature involved simultaneous ozone and total oxidant measurements in the Los Angeles basin by the California Air Resources Board (1978) in 1974, 1976, and 1978. The maximum hourly data pairs were correlated (Chock et al., 1982) and yielded the following regression equation for 1978, in which a large number (927) of data pairs were available:

$$\text{Oxidant (ppm)} = 0.870\ O_3 + 0.005$$
$$\text{(Correlation coefficient} = 0.92) \qquad (4\text{-}19)$$

The oxidant data were uncorrected for NO_2 and SO_2 interferences, and on individual days maximum oxidant averages were both higher than and lower than ozone averages.

In summary, specific ozone measurements agree fairly well with total oxidants corrected for NO_2 and SO_2 interferences, and in such corrected total oxidants measurements ozone is the dominant contributor. Indeed, it is difficult to discern the presence of other oxidants in corrected total oxidant data. Without corrections there can be major temporal discrepancies between ozone and oxidants data, which are primarily a result of oxidizing and reducing interferences with KI measurements. As a result of these interferences, on any given day the total oxidant values may be higher than or lower than simultaneous ozone data. The measurement of ozone is a more reliable indicator than total oxidant measurements of oxidant air quality.

4.4.1.5 Methods for Sampling and Analysis of Peroxyacetyl Nitrate and Its Homologues. Only two analytical techniques have been used to obtain significant data on ambient peroxyacetyl nitrate (PAN) concentrations. These are gas chromatography with electron capture detection (GC-ECD) and long-path Fourier transform infrared (FTIR) spectrometry. Atmospheric data on PAN concentrations have been obtained predominantly by GC-ECD because of its relative simplicity and superior sensitivity. These techniques have been described in this chapter along with attendant methods of sampling, PAN generation, absolute analysis, and calibration.

By far the most widely used technique for the quantitative determination of ppb concentrations of PAN and its homologues is GC-ECD (Darley et al., 1963; Stephens, 1969). With carbowax or SE30 as a stationary phase, PAN, peroxypropionyl nitrate (PPN), peroxybenzoyl nitrate (PBzN), and other homologues (e.g., peroxybutyryl nitrate) are readily separated from components such as air, water, and other atmospheric compounds, as well as ethyl nitrate, methyl nitrate, and other contaminants that are present in synthetic mixtures. Electron-capture detection provides sensitivities in the ppb and sub-ppb ranges. Typically, manual air samples are collected in 50- to 200-ml ungreased glass syringes and purged through the gas-sampling valve. Continuous analyses are performed by pumping ambient air through a gas sampling loop of an automatic valve, which periodically injects the sample onto the column. Samples collected from the atmosphere should be analyzed as soon as possible because PAN and its homologues undergo thermal decomposition in the gas phase and at the surface of containers. The recent work of Singh and Salas (1983a,b) on the measurement of PAN in the free (unpolluted) troposphere (see Chapter 5) is illustrative of current capabilities for measuring low concentrations. A minimum detection limit of 0.010 ppb was obtained.

The literature contains conflicting reports on the effects of variable relative humidity on PAN measurements by GC-ECD. If a moisture effect is suspected in a PAN analysis, the bulk of this evidence suggests that humidification of PAN calibration samples (to a range approximating the humidity of the samples being analyzed) would be advisable.

Conventional long-path infrared spectroscopy and Fourier-transform infrared spectroscopy (FTIR) have been used to detect and measure atmospheric PAN. Sensitivity is enhanced by the use of FTIR. The most frequently used IR bands have been assigned and the absorptivities reported in the literature (Stephens, 1964; Bruckmann and Willner, 1983; Holdren and Spicer, 1984) permit the quantitative analysis of PAN without calibration standards. The absorptivity of the 990 cm^{-1} band of PBzN, a higher homologue of PAN, has been reported by Stephens (1969). Tuazon et al. (1978) describes an FTIR system operable at pathlengths up to 2 km for ambient measurements of PAN and other trace constituents. This system employed an eight-mirror multiple reflection cell with a 22.5-m base path. Tuazon et al. (1981b) reported maximum PAN concentrations ranging from 6 to 37 ppb over a 5-day smog episode in Claremont, CA. Hanst et al. (1982) made measurements with a 1260-m folded optical path system during a 2-day smog episode in Los Angeles in 1980. An upper limit of 1 ppb of PBzN was placed, and the maximum PAN concentration observed was 15 ppb. The large internal surface area of the White cells may serve to promote the decomposition or irreversible adsorption of reactive trace species such as PAN. High volume sampling rates and inert internal surface materials are used to minimize these effects.

Because of the thermal instability of dilute PAN samples and the explosive nature of liquefied PAN, calibration samples are not commercially available and must be prepared. Earlier methods used to synthesize PAN have been summarized by Stephens (1969). The photolysis of alkyl nitrites in oxygen was the most commonly used procedure and may still be used by some investigators. As described by Stephens et al. (1965), the liquefied crude mixture obtained at the outlet of the photolysis chamber is purified by preparative-scale GC. [CAUTION: Both the liquid crude mixture and the purified PAN samples are violently explosive and should be handled behind explosion shields using plastic full-face protection, gloves, and a leather coat at all times.] The pure PAN is usually diluted to about 1000 ppm in cylinders pressurized with nitrogen to 100 psig and stored at reduced temperatures, <15°C.

Gay et al. (1976) have used the photolysis of chlorine: aldehyde: nitrogen dioxide mixtures in air or oxygen for the preparation of PAN and a number of its homologues at high yields. This procedure has been utilized in a portable

PAN generator that can be used for the calibration of GC-ECD instruments in the field (Grosjean, 1983; Grosjean et al., 1984).

Several investigators have recently reported on a condensed-phase synthesis of PAN by nitration of peracetic acid in a hydrocarbon solvent. High yields are produced of a pure product free of other alkyl nitrates (Hendry and Kenley, 1977; Kravetz et al., 1980; Nielsen et al., 1982; Holdren and Spicer, 1984). After the nitration is complete, the hydrocarbon fraction containing PAN concentrations of 2 to 4 mg/ml can be stored at -20°C for periods longer than a year (Holdren and Spicer, 1984).

The most direct method for absolute analysis of these PAN samples is by infrared absorption, using the IR absorptivities mentioned earlier. Conventional IR instruments and 10-cm gas cells can analyze gas standards of concentrations >35 ppm. Liquid microcells can be used for the analysis of PAN in isooctane solutions. The alkaline hydrolysis of PAN to acetate ion and nitrite ion in quantitative yield (Nicksic et al., 1967) provides a means independent of infrared for the quantitative analysis of PAN. Following hydrolysis, nitrite ion may be quantitatively analyzed by the Saltzman colorimetric procedure (Stephens, 1969). The favored procedures now use ion chromatography to analyze for nitrite (Nielsen et al., 1982) or acetate (Grosjean, 1983; Grosjean et al., 1984) ions. Another calibration procedure has been proposed that is based on the thermal decomposition of PAN in the presence of excess and measured NO concentrations (Lonneman et al., 1982). The acetylperoxy radical, $CH_3C(O)O_2$, and its decomposition products rapidly oxidize nitric oxide (NO) to NO_2 with a stoichiometry that has been experimentally determined.

4.4.1.6 Methods for Sampling and Analysis of Hydrogen Peroxide. Hydrogen peroxide (H_2O_2) is significant in photochemical smog as a chain terminator; as an index of the hydroperoxyl radical (HO_2) concentration (Bufalini and Brubaker, 1969; Demerjian et al., 1974); and as a reactant in the aqueous-phase oxidation of SO_2 to SO_4^{-2} and in the acidification of rain (Penkett et al., 1979; Dasgupta, 1980a,b; Martin and Damschen, 1981; Overton and Durham, 1982).

One of the major problems, however, in assessing the role of atmospheric H_2O_2 has been a lack of adequate measurement methodology. Earlier measurements (Gay and Bufalini, 1972a,b; Bufalini et al., 1972; Kok et al., 1978a,b) reporting H_2O_2 concentrations of 0.01 to 0.18 ppm are now believed to be far too high, and to be the result of artifact H_2O_2 formation from reactions of absorbed O_3 (Zika and Saltzman, 1982; Heikes et al., 1982; Heikes, 1984). Maximum tropospheric H_2O_2 concentrations predicted by modeling calculations (Chameides and

Tan, 1981; Logan et al., 1981) and observed in recent field studies (Das et al., 1983) are on the order of 1 ppb.

Almost all of the methods used for the measurement of atmospheric H_2O_2 have used aqueous traps for sampling. Atmospheric O_3, however, which is also absorbed at concentrations much higher than H_2O_2, reacts in the bulk aqueous phase and at surfaces to produce H_2O_2 and thus is a serious interference (Zika and Saltzman, 1982; Heikes et al., 1982; Heikes, 1984). The removal of absorbed O_3 by purging immediately after sample collection may remove or substantially reduce this interference (Zika and Saltzman, 1982; Das et al., 1983). Another problem identified with aqueous sampling is that other atmospheric species (in particular, SO_2) may interfere with the generation of H_2O_2 in aqueous traps and also react with collected H_2O_2 to reduce the apparent concentration measured (Heikes et al., 1982).

Of the techniques that have been used for the measurement of aqueous and gas-phase H_2O_2, only the chemiluminescence and enzyme-catalyzed methods are summarized below. The other techniques are now believed to have inadequate sensitivity and specificity for the atmospheric concentrations actually present. In addition, the use of a tunable diode infrared laser source should eliminate the problem associated with nearby water bands, and this method is currently under investigation for atmospheric measurements (unpublished work in progress, Schiff, 1985).

Hydrogen peroxide in the atmosphere may be detected at low concentrations by the chemiluminescence obtained from copper(II)-catalyzed oxidaton of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) by H_2O_2 (Armstrong and Humphreys, 1965; Kok et al., 1978a,b). This technique as initially employed suffered the interferences from O_3 and SO_2 discussed above for aqueous traps. Das et al. (1982) employed a static version of the method of Kok et al. (1978a) to measure H_2O_2 concentrations in the 0.01 to 1 ppb range. In addition, samples were purged with argon immediately after collection to eliminate, reportedly, the O_3 interference. Recently, a modified chemiluminescence method has been reported which used hemin, a blood component, as a catalyst for the luminol-based H_2O_2 oxidation (Yoshizumi et al., 1984).

The most promising chemical approach employs the catalytic activity of the enzyme horseradish peroxidase (HRP) on the oxidation of organic substrates by H_2O_2. The production or decay of the fluorescence intensity of the substrate or reaction product is measured as it is oxidized by H_2O_2, catalyzed by HRP.

Some of the more widely used substrates have been scopoletin (6-methoxy-7-hydroxyl,2-benzopyrone) (Andreae, 1955; Perschke and Broda, 1961); 3-(p-hydroxyphenyl)propionic acid (HPPA) (Zaitsu and Okhura, 1980); and leuco crystal violet (LCV) (Mottola et al., 1970).

The decrease in the fluorescence intensity of scopoletin is measured as a function of H_2O_2 concentration. Detection limits have been reported to be quite low (10^{-11} M). The chief disadvantage of this approach is that the concentration of H_2O_2 must be within a narrow range to obtain an accurately measureable decrease in fluorescence. Oxidation of LCV produces intensely colored crystal violet, which has a molar absorption coefficient of 10^5 M^{-1} cm^{-1} at the analytical wavelength, 596 nm. The detection limit reported was 10^{-8} M in 5 cm cells. Two quite similar hydrogen donor substrates have been used. Zaitsu and Okhura (1980) employed 3-(p-hydroxyphenyl) propionic acid and more recently the p-hydroxyphenyl acetic acid homologue is being used (Kunen et al., 1983; Dasgupta and Hwang, 1985). The measurement of the fluorescence intensity of the product dimer provides a quite sensitive means for the assay of H_2O_2.

As with O_3, H_2O_2 calibration standards are not commercially available and are usually prepared at the time of use. The most convenient method for preparing aqueous samples containing micromolar concentrations of H_2O_2 is simply the serial dilution of commercial grade 30 percent H_2O_2 (Fisher Analytical Reagent). Techniques for the convenient generation of gas-phase standards are not available. A technique often used for generating ppm concentrations of H_2O_2 in air involves the injection of microliter quantities of 30 percent H_2O_2 solution into a metered stream of air that flows into a Teflon bag. Aqueous and gas-phase samples are then standardized by conventional iodometric procedures (Allen et al., 1952; Cohen et al., 1967).

4.4.2 Measurement of Precursors to Ozone and Other Photochemical Oxidants

4.4.2.1 Nonmethane Organic Compounds. Numerous analytical methods have been employed to determine nonmethane organic compounds (NMOC) in ambient air. Measurement methods for the organic species may be grouped according to three major classifications: nonmethane hydrocarbons, aldehydes, and other oxygenated compounds.

Nonmethane hydrocarbons have been determined primarily by methods that employ a flame ionization detector (FID) as the sensing element. Early methods for the measurement of total nonmethane hydrocarbons did not provide for speciation of the complex mixture of organics in ambient air. These methods, still in use for analysis of total nonmethane organic compounds, are essentially organic carbon analyzers, since the response of the FID detector is essentially proportional to the number of carbon atoms present in the organic molecule (Sevcik, 1975). Carbon atoms bound, however, to oxygen, nitrogen, or halogens give reduced relative responses (Dietz, 1967). The FID detector has been utilized both as a stand-alone continuous detection system (non-speciation analyzers have indicated an overall poor performance of the commercial instruments when calibration or ambient mixtures containing nonmethane organic compounds (NMOC) concentrations less than 1 ppm C were analyzed (e.g., Reckner, 1974; McElroy and Thompson, 1975; Sexton et al., 1982). The major problems associated with the non-speciation analyzers have been summarized in a recent technical assistance document published by the U.S. Environmental Protection Agency (1981). The document also presents ways to reduce some of the existing problems.

Because of the above deficiencies, other approaches to the measurement of nonmethane hydrocarbons are currently under development. The use of gas chromatography coupled to an FID system circumvents many of the problems associated with continuous non-speciation analyzers. This method, however, requires sample preconcentration because the organic components are present at part-per-billion (ppb) levels or lower in ambient air. The two main preconcentration techniques in present use are cryogenic collection and the use of solid adsorbents (McClenny et al., 1984; Jayanty et al., 1982; Westberg et al., 1980; Ogle et al., 1982). The preferred preconcentration method for obtaining speciated data is cryogenic collection. Speciation methods involving cryogenic preconcentration have also been compared with continuous nonspeciation analyzers (e.g., Richter, 1983). Results indicate poor correlation between methods at ambient concentrations below 1 part-per-million carbon (ppm C).

Aldehydes, which are both primary and secondary pollutants in ambient air, are detected by total NMOC and NMHC speciation methods but can not be quantitatively determined by those methods. Primary measurement techniques for aldehydes include the chromotropic acid (CA) method for formaldehyde (Altshuller and McPherson, 1963; Johnson et al., 1981), the 3-methyl-2-benzothiazolene (MBTH) technique for total aldehydes (e.g., Sawicki et al., 1961; Hauser and Cummins, 1964), Fourier-transform infrared (FTIR) spectroscopy (e.g., Hanst et al., 1982; Tuazon et al., 1978, 1980, 1981a), and high-performance liquid chromatography employing 2,4-dinitrophenyl-hydrazine derivatization (HPLC-DNPH) for aldehyde speciation (e.g., Lipari and Swarin, 1982; Kuntz et al., 1980). The CA and MBTH methods utilize wet chemical procedures and spectrophotometric detection. Interferences from other compounds have been reported for both techniques. The FTIR method offers good specificity and direct *in situ* analysis of ambient air. These advantages are offset, however, by the relatively high cost and lack of portability of the instrumentation. On the other hand, the HPLC-DNPH method not only offers good specificity but can also be easily transported to field sites. A few intercomparison studies of the above methods have been conducted and considerable differences in measured concentrations were found. The data base is still quite limited at present, however, and further intercomparisons are needed.

Literature reports describing the vapor-phase organic composition of ambient air indicate that the major fraction of material consists of unsubstituted hydrocarbons and aldehydes. With the exception of formic acid, other oxygenated species are seldom reported. The lack of oxygenated hydrocarbon data is somewhat surprising since significant quantities of these species are emitted into the atmosphere by solvent-related industries and since at least some oxygenated species appear to be emitted by vegetation. In addition to direct emissions, it is also expected that photochemical reactions of hydrocarbons with oxides of nitrogen, O_3, and hydroxyl radicals will produce significant quantities of oxygenated species. Difficulties during sample collection and analysis may account for the apparent lack of data. Attempts have been made to decrease adsorption by deactivating the reactive surface or by modifying the compound of interest (Osman et al., 1979; Westberg et al., 1980). Additional research efforts should focus on this area.

4.4.2.2 Nitrogen Oxides. Aside from the essentially unreactive nitrous oxide (N_2O), only two oxides of nitrogen occur in ambient air at appreciable concentrations: nitric oxide (NO) and nitrogen dioxide (NO_2). Both compounds, together designated as NO_x, participate in the cyclic reactions in the atmosphere that lead to the formation of ozone. Other minor reactive oxides of nitrogen in ambient air include peroxyacyl nitrates, nitrogen trioxide, dinitrogen pentoxide, and peroxynitric acid.

The preferred means (Federal Reference Method) of measuring NO and NO_2 is the chemiluminescence method (F.R., 1976c). The measurement principle is the gas-phase chemiluminescent reaction of O_3 and NO (Fontijn et al., 1970).

While NO is determined directly in this fashion, NO_2 is detected indirectly by first reducing or thermally decomposing the gas quantitatively to NO with a converter. The reaction of NO and O_3 forms excited NO_2 molecules that release light energy that is proportional to the NO concentration. Although the NO chemiluminescence is interference-free, other nitrogen compounds do interfere when directed through the NO_2 converter. The magnitude of these interferences is dependent upon the type of converter used (Winer et al., 1974; Joshi and Bufalini, 1978). The detection limit of commercial chemiluminescence instruments for NO_2 measurement is 2.5 $\mu g/m^3$ (0.002 ppm) (Katz, 1976).

Development of an instrument based on the chemiluminescent reaction of NO_2 with luminol (5-amino-2, 3-dihydro-1, 4-phthalazine dione) has been reported by Maeda et al. (1980). Wendel et al. (1983) have reported modifications of this luminol-based method in which better response time and less interference from O_3 have been achieved.

Other acceptable methods for measuring ambient NO_2 levels, including two methods designated as equivalent methods, are the Lyshkow-modified Griess-Saltzman method, the instrumental colorimetric Griess-Saltzman method, the triethanolamine method, the sodium arsenite method, and the TGS-ANSA method [TGS-ANSA = triethanolamine, guaiacol (o-methoxyphenol), sodium metabisulfite, and 8-anilino-1-naphthalene sulfonic acid]. The sodium arsenite method and the TGS-ANSA method were designated as equivalent methods in 1977. For descriptions of these methods, the reader is referred to the EPA criteria document for nitrogen oxides (U.S. Environmental Protection Agency, 1982). While some of these methods measure the species of interest directly, others require oxidation, reduction, or thermal decomposition of the sample, or separation from interferences, before measurement. None of these other techniques, however, is widely used to monitor air quality.

Careful adherence to specified calibration procedures is essential for obtaining accurate NO_x measurements. The U.S. Environmental Protection Agency (1975) has issued a technical assistance document that describes in detail the two acceptable calibration methods for NO_x: (1) the use of standard reference materials (SRMs) and (2) gas-phase titration (GPT) of NO with O_3. The SRM for NO is a cylinder of compressed NO in N_2; the mixture is both accurate and stable (Hughes, 1975). The SRM for NO_2 is the NO_2 permeation tube (O'Keeffe and Ortman, 1966; Scaringelli et al., 1970). The gas-phase titration, described by Rehme et al. (1974), is based upon the bimolecular reaction of NO with O_3 to form NO_2 plus O_2. The U.S. Environmental Protection Agency (1975) recommends the combined use of GPT plus SRM procedures, using one technique to check the other.

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5. CONCENTRATIONS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS IN AMBIENT AIR

5.1 INTRODUCTION

The data presented in this chapter on the concentrations of ozone and other photochemical oxidants in ambient air are intended to support and complement information presented in subsequent chapters on the effects of these compounds. Thus, this chapter describes potential exposures of human populations, crops and other vegetation, ecosystems, and nonbiological materials in general terms for the entire nation and in specific terms for selected areas of the country. Since the health and welfare effects of ozone have been much more thoroughly documented than those of other related oxidants, primary emphasis in this chapter is placed on the concentrations of ozone found in ambient air. Potential exposures are described by presenting data on peak and average concentrations nationwide and on seasonal and diurnal patterns in selected urban and nonurban areas. The recurrence on consecutive days of selected levels of ozone has been examined for a few urban sites to aid in understanding the significance of health effects documented in subsequent chapters. Likewise, data have been included that portray representative urban and rural concentrations by season and by time of day. Spatial variations in ozone concentrations are briefly addressed since the effects on concentrations of latitude, altitude, intracity variations, and indoor-outdoor gradients are pertinent to the assessment of potential exposures of human populations, and, except for the indoor-outdoor gradients, of crops and other vegetation and ecosystems.

Ozone is the only photochemical oxidant other than nitrogen dioxide that is routinely monitored and for which a comprehensive aerometric data base exists. Data for peroxyacetyl nitrate (PAN) and its homologues and for hydrogen peroxide (H_2O_2) and formic acid (HCOOH) have all been obtained as part of special research investigations. Consequently, no data on nationwide patterns of occurrence are available for these non-ozone oxidants; nor are extensive data available on the correlations of levels and patterns of these oxidants with those of ozone. Data on these oxidants are considerably more abundant now, however, than in 1978, when the previous criteria document for ozone and other photochemical oxidants was published (U.S. Environmental Protection Agency, 1978). Sections 5.6 and 5.7 summarize the available data on these other oxidants.

The concentrations of ozone and related photochemical oxidants observed in ambient air are the net result, as shown in Chapter 3, of various combinations of a variety of atmospheric processes, including:

1. Local photochemical production from oxides of nitrogen and reactive volatile organic compounds.
2. Atmospheric mixing after sunrise, such that ozone-rich air from above the nocturnal inversion layer is mixed to the surface, resulting in a steady increase in ozone during the morning and early afternoon. This increase, from ozone preserved aloft, is independent of photochemistry, occurring even in the absence of precursors and photochemical processes.
3. Transport of ozone produced photochemically but not locally.
4. Intrusion into the troposphere, even to ground level, of ozone-rich air from the stratospheric reservoir.
5. Formation of ozone photochemically in the mid-troposphere, with subsequent intrusion into the boundary layer.
6. Chemical scavenging in the atmosphere of ozone and other oxidants; e.g., the reaction of ozone with nitric oxide (NO) or the reaction of H_2O_2 with sulfur dioxide (SO_2).
7. Physical scavenging in the atmosphere of ozone and other oxidants; e.g., the temperature-dependent decomposition of PAN, the precipitation scavenging of H_2O_2, and the photolytic dissociation of ozone.
8. Combined physical and chemical scavenging processes at the surface of the earth; e.g., the deposition of ozone on reactive biological or nonbiological surfaces, such as vegetation, soils, or certain polymers.

These processes include, obviously, both manmade and natural processes and driving mechanisms. The occurrence of high ozone concentrations is most commonly associated with recognized meteorological conditions that involve intense sunlight and elevated temperatures, and the variety of processes involved contribute to strong diurnal cycles. Peak concentrations have been observed to occur, however, at almost any time of day. Ozone may be transported after its formation for distances up to 1000 km or more (e.g., Hov et al., 1978; Wolff and Lioy, 1980). As a result, high concentrations of ozone and related oxidants occur not only near large sources of precursors but also in downwind nonurban areas, and usually later in the day at these downwind receptor sites. Ozone, and apparently PAN, as well, can be transported at night above the surface pollutant and nocturnal inversion layer (Chapter 3), but during daylight hours can be transported considerable distances at or near ground level (Coffey and Stasiuk; 1975a,b).

The emphasis of this chapter is on the documentation of concentrations rather than on explanations of possible causes of observed concentrations. Probable causes and explanations are mentioned, however, where they are pertinent to the discussion.

Most of the data presented in this chapter to characterize both nationwide and site-specific ozone concentrations in ambient air were obtained after 1978. Two factors influenced the use of post-1978 data. First, the current Federal Reference Method for ozone, chemiluminescence, and the equivalent UV method were almost universally employed by 1979. Second, EPA promulgated a UV calibration method for ozone in 1979. Thus, these data form a relatively homogeneous set for purposes of intercomparison. Because of the well-recognized difficulties in converting from older data sets to the current reference method, few pre-1979 aerometric data for ozone are presented in this chapter, and then only to demonstrate spatial variations in concentrations that are pertinent to exposure assessments.

5.2 TRENDS IN NATIONWIDE OZONE CONCENTRATIONS

Whether ozone concentrations in ambient air are static, rising, or declining over time must be determined from statistical tests using comparable aerometric data for a number of years. The national trend in ozone concentrations is shown in Figure 5-1 for the 9-year period, 1975 through 1983 (U.S. Environmental Protection Agency, 1984a). The concentrations depicted are the average second-highest 1-hour concentrations for selected stations for each year. In this context, the second-highest 1-hour value for each station is selected from all daily maximum 1-hour values ($n \leq 365$) recorded per year at that station. Subsequently, this statistic will be referred to as the second-highest daily maximum 1-hour value or simply the second-highest 1-hour value. The 176 monitoring stations included in this analysis reported at least 50 percent of the possible hourly values for the ozone season in at least 7 of these 9 years. (The ozone season varies at the respective sites from 4 to 12 months, depending upon local conditions. The sampling period is specified in State Implementation Plans.)

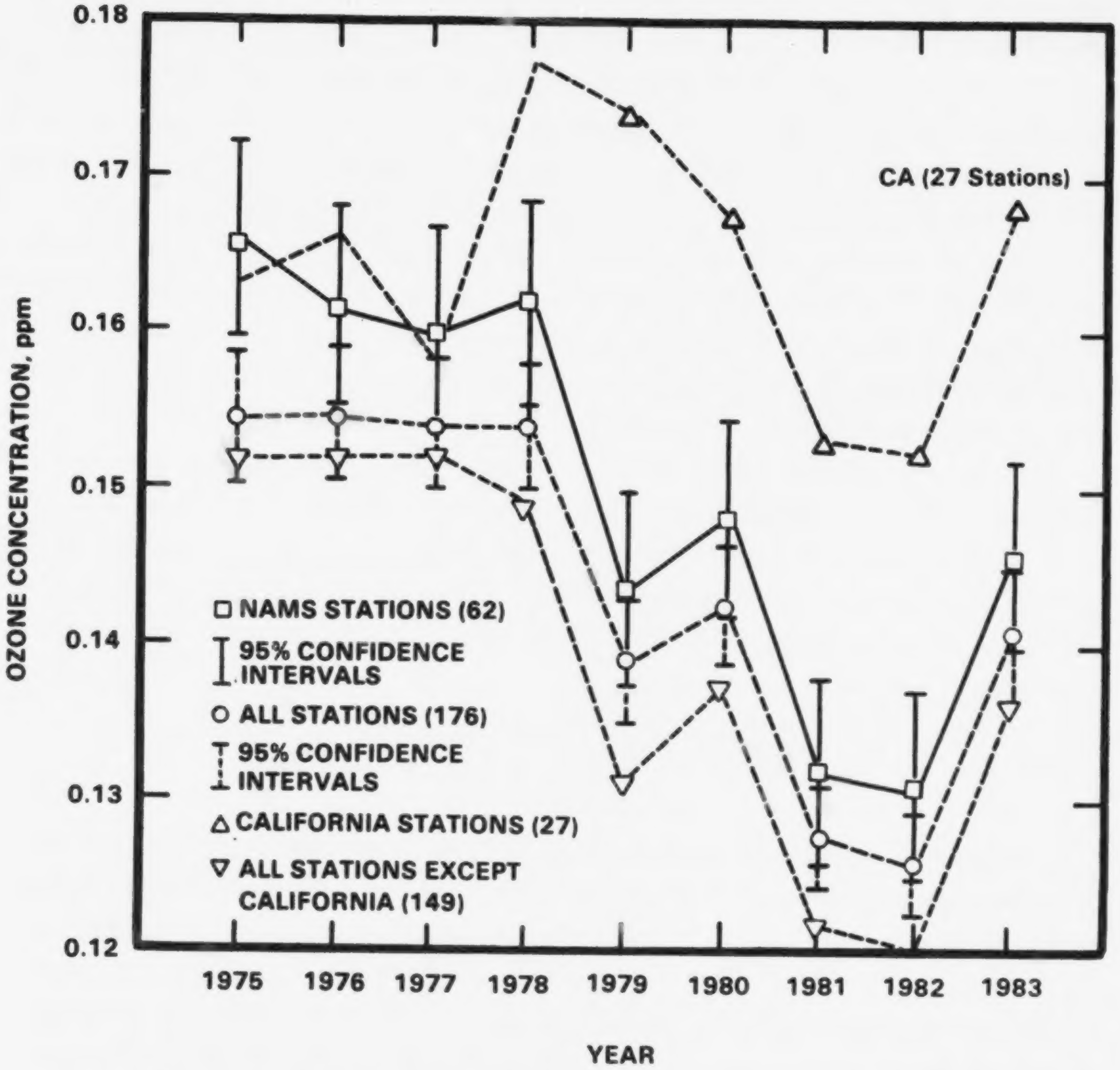


Figure 5-1. National trend in composite average of the second highest value among daily maximum 1-hour ozone concentrations at selected groups of sites, 1975 through 1983.

Source: U.S. Environmental Protection Agency (1984a).

Ambient air monitoring stations in the nation are generally operated by state and local agencies, but among the stations is a small group of National Air Monitoring Stations (NAMS) whose data are reported directly to EPA. The trend line for the subset of the 62 NAMS ozone stations, also shown in Figure 5-1, tracks fairly closely the trend for all 176 stations. To permit a comparison of aerometric data for California, a high-oxidant area, with the nationwide trends data, data for California and data for all states other than California are also plotted separately in Figure 5-1 and are compared below.

For the entire 9-year period, 1975 through 1983, all subsets of monitoring stations show a decline in the composite second-highest daily maximum 1-hour ozone concentration. In 1979, a new, more accurate ozone calibration procedure was promulgated by the U.S. Environmental Protection Agency (see Chapter 4). Between 1979 and 1982, a small decline of 9 to 10 percent in nationwide ozone concentrations occurred. From 1982 to 1983, however, concentrations increased by about 10 percent in California, by about 12 percent nationwide, and by about 14 percent outside California. Recently published data for 1984 from a somewhat smaller number of stations (163 sites), not depicted in Figure 5-1, show a decrease in second-highest 1-hour concentrations nationwide, with ozone levels in 1984 approximating those recorded in 1981, which are shown in Figure 5-1 (U. S. Environmental Protection Agency, 1986).

Note the influence of ozone data from Calfornia. The California data heavily influence the trends data because of the number of California monitoring sites represented in the data and because of the actual concentrations of ozone in California.

Evaluation of national trends, as well as local or regional trends, in reported concentrations of ozone in ambient air over the past 5 to 10 years is complicated by a number of factors, including: (1) the change in calibration procedure recommended by EPA in 1978 and promulgated in 1979 (see Chapter 4); (2) the possible effects on aerometric data of quality assurance procedures instituted by EPA in 1979; (3) the influence of diverse regional meteorological conditions; and (4) changes in precursor emissions.

How much of the observed decline in ozone concentrations from 1975 through 1982 is attributable to the 1979 promulgation of the ultraviolet (UV) calibration method as the Federal Reference Method is uncertain. To determine that, the monitoring practices at each of the 176 sites would have to be examined in detail to find out the calibration methods used, the date when the UV method was adopted for this site, and whether states applied correction factors to prior data (see, e.g., Walker, 1985; Hoggan, 1986; Walker, 1986). Such an examination would be necessary because not all monitoring sites switched to the use of the UV method simultaneously. For example, the state of California (in EPA Region IX) had already been using the UV method before it was promulgated in February 1979. In addition, other states, in other regions, may have used the boric acid-potassium iodide (BAKI) method before, after, or both before and after promulgation of the UV method, since the BAKI procedure was allowed by EPA as an interim method for 18 months following the 1979 UV promulgation (see Chapter 4). Likewise, other states used gas-phase titration prior to 1979 but either BAKI or UV procedures following the UV promulgation. In addition, random errors associated with individual operator practices occur. Thus, the relationships among these three methods, even if monitoring practices at individual sites were known, are complex and would preclude the simple application of a single correction factor to these trend data (see Chapter 4).

Hunt and Curran (1982) have noted that only EPA Region IX showed improvement in ozone air quality between 1979 and 1981 but, in contrast to other EPA regions, showed no improvement in that period versus the 1975 to 1979 period. Since California, which dominates Region IX, changed its calibration method in 1975, the decrease in ozone concentrations seen in California from 1979 through 1982 (Figure 5-1) cannot be attributed to the introduction of the UV calibration method. The shape of the trend line for California is quite similar to that for the rest of the nation over the 4-year period (1980 through 1983) following the promulgation of the UV method. From 1982 to 1983, an increase in ozone concentrations occurred nationwide, with the percentage increase in California roughly paralleling that for the rest of the nation. Increased precursor emissions and meteorological conditions conducive to oxidant formation appear to be the most likely causes of the increase in 1983 in the composite average of the second-highest daily maximum 1-hour ozone concentrations. An examination of emissions data, however, indicates that NO_x emissions did not change significantly from 1982 to 1983 and that VOC emissions rose only 3 percent in that period (U.S. Environmental Protection Agency, 1984b; also see Chapter 3). Therefore, precursor emissions are not thought to account for all of the 12 percent increase in O_3 from 1982 to 1983 nationwide (U.S. Environmental Protection Agency, 1984a).

The influence of meteorological conditions on ozone concentrations has been explored for 10 cities using an experimental index based on meteorological parameters conducive to ozone formation (U.S. Environmental Protection Agency, 1984a). The index suggests that the potential for ozone formation was greater in 1983 than in 1981 and 1982; however, the index also indicates that even greater potential for ozone formation existed in 1980 than in 1983 and that conditions in 1979 might be comparable to those in 1981 and 1982. Thus, this simple index may indicate the direction but not the magnitude of the effects of meteorological factors on ozone formation.

From a study of climate in the upper Midwest during the summer of 1983, Wendland et al. (1984) have reported that temperatures, which correlate reasonably well with insolation, were generally higher in the summer of 1983 than the 1950-through-1980 norm for the 12-state region; and that cooling-degree days over about one-third of the region were 50 percent higher than normal. While not quantitative or conclusive, these studies do suggest that meteorological conditions in 1983 contributed to the increase in the second-highest value among daily maximum 1-hour ozone concentrations.

Trends in the composite average second-highest daily maximum 1-hour ozone values in the 10 EPA regions are shown in Figure 5-2 (U.S. Environmental Protection Agency, 1984a). The use of data beginning with 1979 avoids some of the potential effects of changes in calibration and quality assurance procedures mentioned earlier. Nine of the 10 regions show a 7 to 15 percent decrease in this statistic from the 1979-1980 period to the 1981-1982 period. The same nine regions showed increases of 6 to 16 percent from the 1981-1982 period to 1983, demonstrating the pervasiveness of the trend. Only in the Pacific Northwest, Region X, was there an opposite trend: +6 percent in 1981-1982 and -9 percent in 1983.

5.3 OVERVIEW OF OZONE CONCENTRATIONS IN URBAN AREAS

An overview of nationwide urban ozone concentrations for 1981 is provided in Figures 5-3 and 5-4, which depict graphically the average daylight concentrations. Figure 5-3 shows data for spring and summer months, the months that make up the smog season in most though not all areas of the nation; and Figure 5-4 shows daylight concentrations during the fall and winter months. The daylight period of 6:00 a.m. to 8:00 p.m. includes the hours of greatest human activity

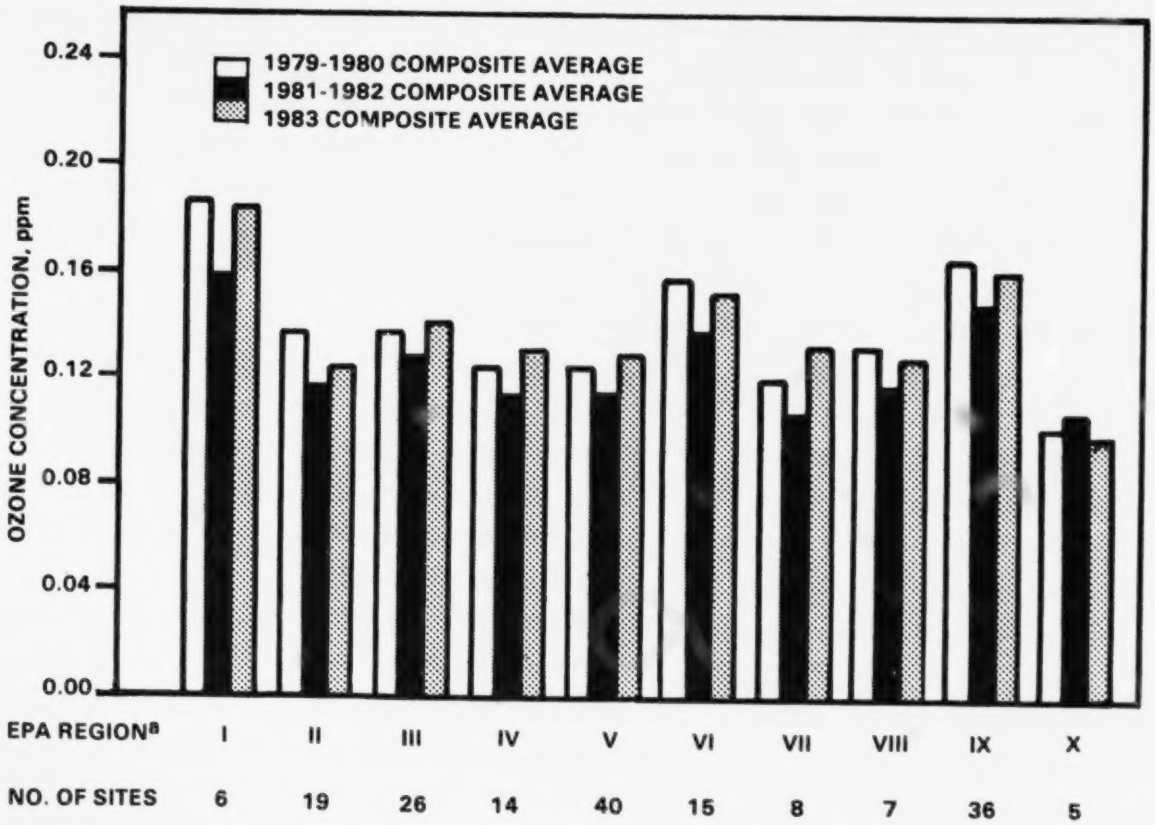
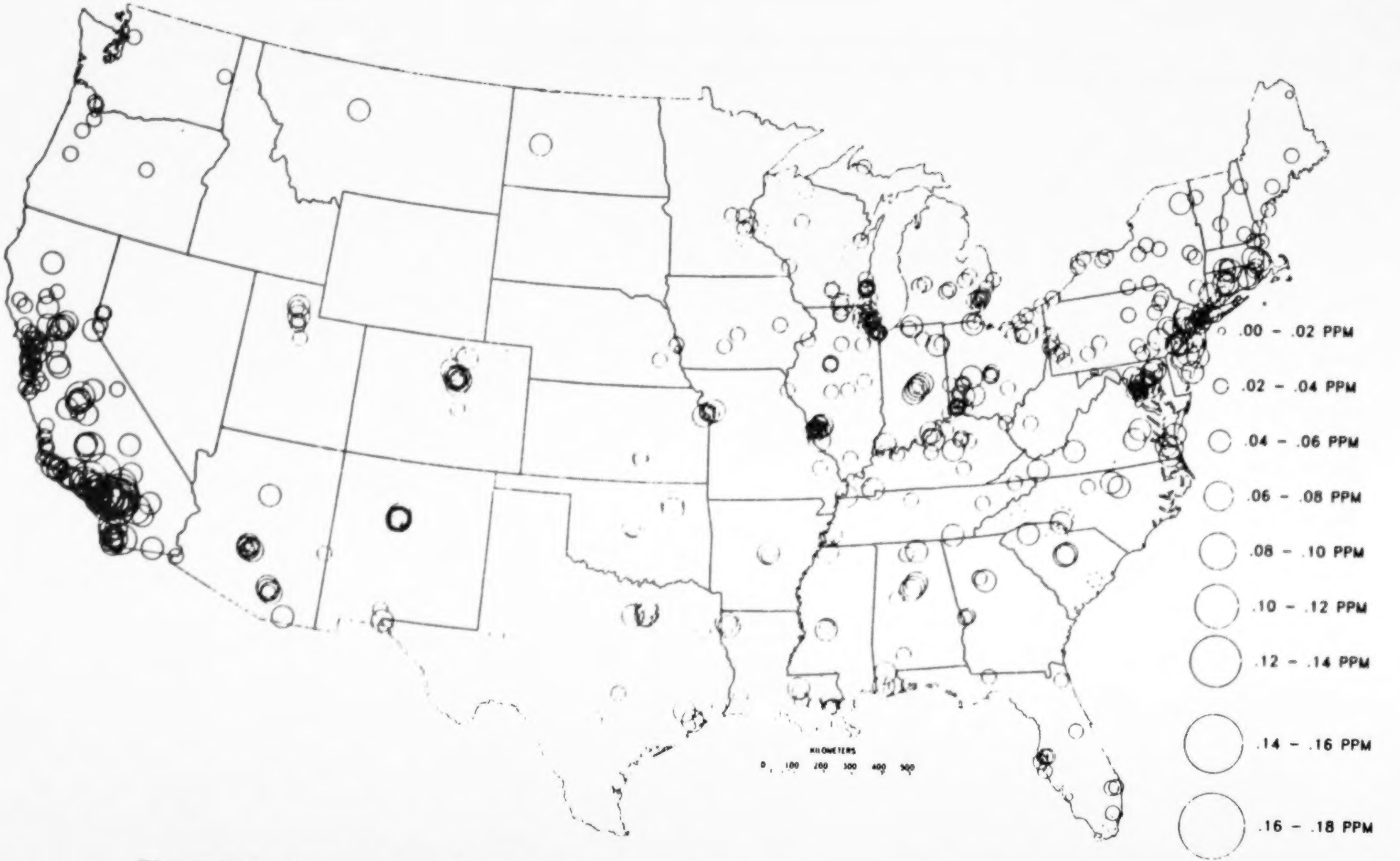


Figure 5-2. Comparison of the 1979-1980, 1981-1982, and 1983 composite average of the second highest daily maximum 1-hour ozone concentrations across EPA Regions.

[a]Note: Regions are composed of the following states:

I CT, MA, ME, NH, RI, VT
II NJ, NY, PR, VI
III DE, MD, PA, VA, WV
IV AL, FL, GA, KY, MS, NC, SC, TN
V IL, IN, MI, MN, OH, WI
VI IA, KS, MO, NE
VII AR, LA, NM, OK, TX
VIII CO, MT, ND, SD, UT, WY
IX AZ, CA, HI, NV
X AK, ID, OR, WA

Source: U.S. Environmental Protection Agency (1984a).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.10 - .12 PPM
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.14 - .16 PPM
.16 - .18 PPM
KILOMETERS
0 100 200 300 400 500

Figure 5-3. Average daylight (6:00 a.m. to 8:00 p.m.) concentrations of ozone in the second and third quarters (April through September), 1981.

01 Apr 1983

Source: SAROAD (1985d). Derived by G. Duggan, OAQPS.

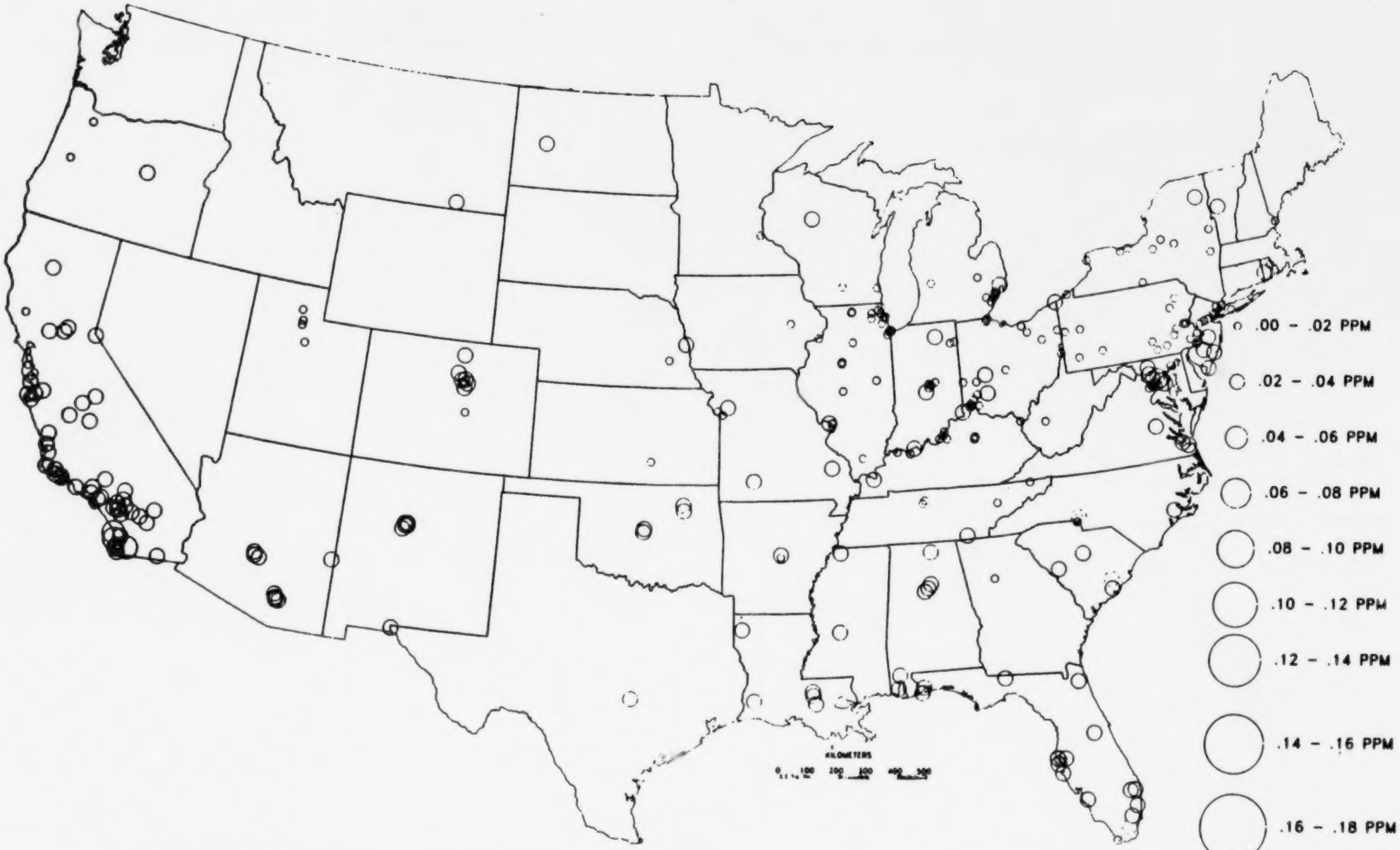
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Figure 5-4. Average daylight (6:00 a.m. to 8:00 p.m.) concentrations of ozone in the first and fourth quarters (January through March and October through December), 1981.

01 Apr 1983

Source: SAROAD (1985d). Derived by G. Duggan, OAQPS.

outdoors; the hours when exposure of vegetation and ecosystems would be expected to have the greatest consequences (stomata are open in daylight and photosynthesis is taking place; see Chapter 6); and the hours of greatest local formation of ozone and other oxidants via photochemistry in the atmosphere (see Chapter 3). The average concentrations during the spring and summer months (second and third quarters of the year) are clustered mainly in the 0.04 to 0.06 ppm range. Averages for the winter and fall months (first and fourth quarters) are clustered mainly in the 0.02 to 0.04 ppm range.

The stations used in Figures 5-3 and 5-4 reported at least 75 percent of the possible 1-hour values per quarter. Some stations, however, monitor ozone only during the months when the potential for photochemical ozone formation is significant in those localities. Also, certain areas of the United States are not monitored routinely for ozone because of the lack of emission sources or transport events and thus the low potential for significant ozone or oxidant concentrations. The Great Basin and the Great Plains, for example, are such areas.

Figure 5-5 shows the nationwide frequency distributions of the first-, second-, and third-highest 1-hour O_3 concentrations at predominantly urban stations aggregated for 1979, 1980, and 1981, as well as the highest 1-hour O_3 concentration at sites of the National Air Pollution Background Network (NAPBN) (see Section 5.4.1) aggregated for the same 3 years. Only data collected by the Federal Reference Method (chemiluminescence) or the equivalent UV method (see Chapter 4) have been used in this analysis. A "valid site" is one reporting at least 75 percent of the 8760 possible 1-hour values in a year. There were 282 such sites in 1979, 266 in 1980, and 358 in 1981 (U.S. Environmental Protection Agency, 1980, 1981, 1982a). As shown by Figure 5-5, 50 percent of the second-highest 1-hour values from non-NAPBN sites in this 3-year period were 0.12 ppm or less and about 10 percent were equal to or greater than 0.20 ppm. At the NAPBN sites, the collective 3-year distribution (1979 through 1981) is such that about 60 percent of the values are less than 0.10 ppm and fewer than 20 percent are higher than 0.12 ppm.

Table 5-1 lists the second-highest 1-hour O_3 values reported for 1981 through 1983 for the 80 most populous Standard Metropolitan Statistical Areas (SMSAs), grouped by population (see Table 5-1 for a definition of the "second-highest" values). Collectively these SMSAs account for about 53 to 54 percent of the 1981 United States population of 229.3 million. The significant observation to be drawn from this table of second-highest values is that the lowest

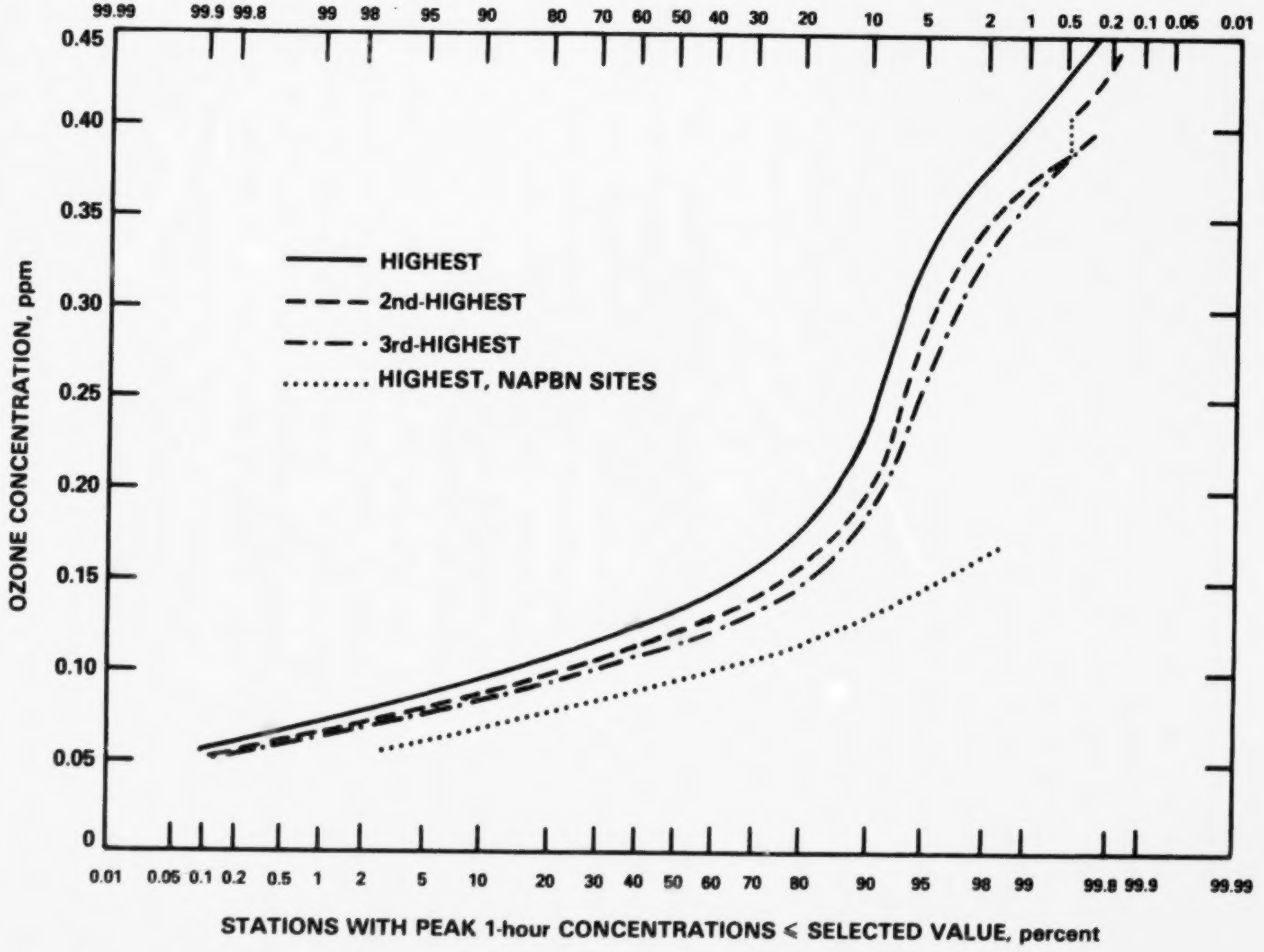


Figure 5-5. Distributions of the three highest 1-hour ozone concentrations at valid sites (906 station-years) aggregated for 3 years (1979, 1980, and 1981) and the highest ozone concentrations at NAPBN sites aggregated for those years (24 station-years). Source: U.S. Environmental Protection Agency (1980, 1981, 1982).

TABLE 5-1. SECOND-HIGHEST 1-hr OZONE CONCENTRATIONS[a,b] REPORTED FOR STANDARD METROPOLITAN STATISTICAL AREAS HAVING POPULATIONS $\geq$0.5 MILLION, 1981 THROUGH 1983

Standard Metropolitan Statistical Area	Ozone concentration, ppm		
	1981	1982	1983
Population >2 million			
New York, NY - NJ	0.18	0.17	0.19
Los Angeles - Long Beach, CA	0.35	0.32	0.37
Chicago, IL	0.14	0.12	0.17
Philadelphia, PA - NJ	0.17	0.18	0.10
Detroit, MI	0.15	0.16	0.17
San Francisco - Oakland, CA	0.14	0.14	0.17
Washington, DC - MD - VA	0.15	0.15	0.17
Dallas - Fort Worth, TX	0.15	0.17	0.16
Houston, TX	0.23	0.21	0.28
Boston, MA	0.13	0.16[c]	0.18
Nassau - Suffolk, NY	0.14	0.13	0.17
St. Louis, MO - IL	0.15	0.16	0.18
Pittsburgh, PA	0.16	0.14	0.14
Baltimore, MD	0.17	0.14	0.19
Minneapolis - St. Paul, MN - WI	0.10	0.10	0.13
Atlanta, GA	0.14	0.14	0.17
Summary statistics:			
Minimum 1-hour value	0.10	0.10	0.10
Median 1-hour value	0.15	0.15	0.17
Maximum 1-hour value	0.35	0.32	0.37
Population 1 to < 2 million			
Newark, NJ	0.14	0.17	0.25
Anaheim - Santa Ana - Garden Grove, CA	0.31	0.18[c]	0.28
Cleveland, OH	0.12	0.13	0.15
San Diego, CA	0.24	0.21	0.20
Miami, FL	0.14	0.14	0.12
Denver - Boulder, CO	0.13	0.14	0.14
Seattle - Everett, WA	0.12	0.09	0.10
Tampa - St. Petersburg, FL	0.12	0.12	0.14
Riverside - San Bernardino - Ontario, CA	0.34	0.32	0.34
Phoenix, AZ	0.16	0.12	0.16
Cincinnati, OH - KY - IN	0.13	0.13	0.15
Milwaukee, WI	0.17	0.13	0.18
Kansas City, MO - KS	0.12	0.10	0.13
San Jose, CA	0.14	0.14	0.16
Buffalo, NY	0.12[c]	0.11	0.12
Portland, OR - WA	0.15	0.12	0.12
New Orleans, LA	0.12	0.17	0.12
Indianapolis, IN	0.13	0.12	0.14
Columbus, OH	0.11	0.13	0.12

TABLE 5-1 (continued). SECOND-HIGHEST 1-hr OZONE CONCENTRATIONS[a,b] REPORTED FOR STANDARD METROPOLITAN STATISTICAL AREAS HAVING POPULATIONS $\geq$0.5 MILLION, 1981 THROUGH 1983

Standard Metropolitan Statistical Area	Ozone concentration, ppm		
	1981	1982	1983
San Juan, PR	0.07	0.04[c]	ND[d]
San Antonio, TX	0.12	0.14	0.12
Fort Lauderdale - Hollywood, FL	0.11	0.09	0.10
Sacramento, CA	0.17	0.16	0.15
Summary statistics:			
Minimum 1-hour value	0.07	0.04	0.10
Median 1-hour value	0.13	0.13	0.14
Maximum 1-hour value	0.34	0.32	0.34
Population 0.5 to < 1 million			
Rochester, NY	0.12	0.11	0.12
Salt Lake City - Ogden, UT	0.16	0.14	0.14
Providence - Harwick - Pawtucket, RI - MA	0.15	0.15	0.15
Memphis, TN - AR - MS	0.14	0.13	0.15
Louisville, KY - IN	0.14	0.14	0.16
Nashville - Davidson, TN	0.13	0.11	0.12
Birmingham, AL	0.16	0.15	0.15
Oklahoma City, OK	0.11	0.11[c]	0.11
Dayton, OH	0.13	0.16	0.13
Greensboro - Winston-Salem - High Point, NC	0.11	0.11	0.12
Norfolk - Virginia Beach - Portsmouth, VA - NC	0.12	0.11	0.13
Albany - Schenectady - Troy, NY	0.12	0.12	0.12
Toledo, OH - MI	0.13	0.13	0.13
Honolulu, HI	0.05	0.07	0.06
Jacksonville, FL	0.11	0.12	0.14
Hartford, CT	0.15	0.17	0.19
Orlando, FL	0.10	0.10[c]	0.11
Tulsa, OK	0.15	0.13	0.13
Akron, OH	0.24[e]	0.14	0.13
Gary - Hammond - East Chicago, IN	0.14	0.13	0.17
Syracuse, NY	0.11	0.12	0.08
Northeast Pennsylvania	0.10	0.16	0.13
Charlotte - Gastonia, NC	0.12	0.12	0.15
Allentown - Bethlehem - Easton, PA - NJ	0.12	0.15	0.14
Richmond, VA	0.12	0.12	0.14
Grand Rapids, MI	0.11	0.11	0.14
New Brunswick - Perth Amboy - Sayreville, NJ	0.13	0.16	0.19
West Palm Beach - Boca Raton, FL	0.09	0.09	0.09
Omaha, NE - IA	0.08	0.09	0.09
Greenville - Spartanburg, SC	0.11	0.11	0.11
Jersey City, NJ	0.14	0.14	0.16
Austin, TX	0.12	0.11	0.12

TABLE 5-1 (continued). SECOND-HIGHEST 1-hr OZONE CONCENTRATIONS[a,b] REPORTED FOR STANDARD METROPOLITAN STATISTICAL AREAS HAVING POPULATIONS ≥0.5 MILLION, 1981 THROUGH 1983

Standard Metropolitan Statistical Area	Ozone concentration, ppm 1981	1982	1983
Youngstown - Warren, OH	0.13	0.11	0.11
Tucson, AZ	0.10	0.12	0.11
Raleigh - Durham, NC	0.12	0.09	0.13
Springfield - Chicopee - Holyoke, MA - CT	0.16	0.16	0.19
Oxnard - Simi Valley - Ventura, CA	0.20	0.22	0.21
Wilmington, DE - NJ - MD	0.12[c]	0.16	0.18
Flint, MI	0.11	0.11	0.11
Fresno, CA	0.17	0.16	0.16
Long Branch - Asbury Park, NJ	ND[d]	ND[d]	ND[d]
Summary statistics:			
Minimum 1-hour value	0.05	0.07	0.06
Median 1-hour value	0.12	0.12	0.13
Maximum 1-hour value	0.24	0.22	0.21

[a] The maximum 1-hour value for each day forms the data set from which the highest and "second-highest" concentrations are determined. Thus, the "second-highest" 1-hour concentration occurs on a different day from the highest and therefore is not necessarily the absolute second-highest concentration for the monitoring period.

[b] These values permit a comparison of potential exposures and are not necessarily equivalent to the "design value" used for control strategy development.

[c] Less than 50% of days in ozone season.

[d] ND = no data.

[e] Questionable data; third-highest value for 1981 was 0.125 ppm.

Source: U.S. Environmental Protection Agency (1984a).

median concentrations in 1981, 1982, and 1983, for SMSAs having populations of 0.5 to 1 million, are 0.12, 0.12, and 0.13 ppm, values that equal or exceed the current national ambient air quality standard for ozone. With the possible exception of the concentration reported for Akron, Ohio, in 1981, which appears to be questionable (see footnote, Table 5-1), the highest of all the second-highest 1-hour concentrations in these 80 SMSAs occurred in California in all 3 years.

5.4 OVERVIEW OF OZONE CONCENTRATIONS IN NONURBAN AREAS

As mentioned in the preceding section, very few ozone monitoring stations are located in nonurban areas. Consequently, the aerometric data base for nonurban areas is not comparable to that for urban areas. The nonurban data presented in this section were obtained from two special-purpose monitoring networks that were designed to measure ozone concentrations at sites specifically selected to represent a variety of pristine, rural, or suburban environments. These sites do not all represent areas totally unaffected by manmade ozone or its precursors, as shown by the fact that some data records contain a significant number of high values that are best explained as resulting from the transport of ozone or its precursors from upwind urban areas. The data given here are intended to show an overview of nonurban concentrations in areas with relatively infrequent urban influences. Additional data on specific rural areas are presented in Sections 5.5.1 and 5.5.2.

5.4.1 National Air Pollution Background Network (NAPBN)

The NAPBN consists of eight stations located in eight National Forests (NF) across the country (Figure 5-6). The first three stations began operation in 1976 (Green Mountain NF, Vermont; Kisatchie NF, Louisiana; and Custer NF, Montana); the second three in 1978 (Chequamegon NF, Wisconsin; Mark Twain NF, Missouri; and Croatan NF, North Carolina); and the last two in 1979 (Apache NF, Arizona; and Ochoco NF, Oregon). Yearly summaries of ozone concentrations through 1980 are shown in Table 5-2 for the three sites established first (Evans et al., 1983). The principal points of interest in these summary statistics are the range and the arithmetic mean of the ozone concentrations measured at these National Forest sites. The arithmetic mean concentrations for the three sites ranged from 0.027 ± 0.015 ppm at the Kisatchie NF site in

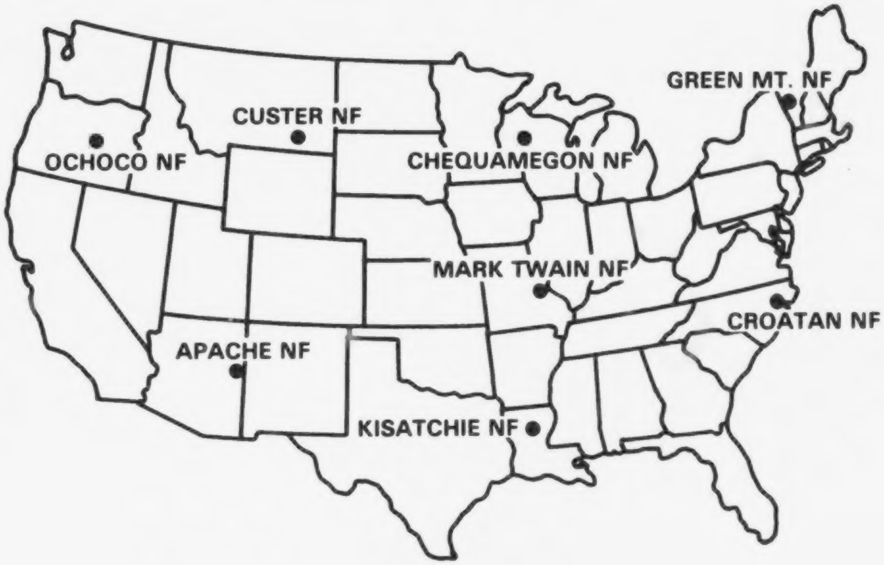

GREEN MT. NF
CUSTER NF
OCHOCO NF
CHEQUAMEGON NF
MARK TWAIN NF
CROATAN NF
APACHE NF
KISATCHIE NF

Figure 5-6. Locations of the eight national forest (NF) stations constituting the National Air Pollution Background Network (NAPBN).

Source: Evans et al. (1983).

TABLE 5-2. ANNUAL OZONE SUMMARY STATISTICS FOR THREE SITES OF THE NATIONAL AIR POLLUTION BACKGROUND NETWORK

Site	Year	No. 1-hr meas.	% of possible 1-hr meas.	Concn., ppm		Concn., ppm		Concn., ppm	
				Min.	Max.	Arith. mean	Arith. std. dev.	Geom. mean	Geom. std. dev.
Kisatchie NF, LA	1976	3448	39.4	ND[a]	0.125	0.032	0.021	0.024	2.19
	1977	6793	77.5	ND	0.135	0.033	0.023	0.025	2.25
	1978	5636	64.3	ND	0.125	0.034	0.021	0.027	2.14
	1979	6993	79.8	ND	0.100	0.027	0.015	0.023	1.92
	1980	4438	50.7	ND	0.105	0.028	0.016	0.023	1.94
Custer NF, MT	1976	275	3.1	0.020	0.060	0.039	0.008	0.038	1.22
	1977	7603	86.8	ND	0.080	0.040	0.011	0.039	1.37
	1978	7674	87.6	ND	0.075	0.030	0.017	0.023	2.14
	1979	8488	96.9	ND	0.070	0.032	0.012	0.029	1.59
	1980	7754	88.5	ND	0.070	0.037	0.012	0.035	1.41
Green Mt. NF, VT	1976	1058	12.1	ND	0.060	0.029	0.011	0.026	1.76
	1977	6483	74.0	ND	0.145	0.038	0.021	0.031	2.00
	1978	3671	41.9	ND	0.105	0.029	0.018	0.024	2.01
	1979	6423	73.3	ND	0.105	0.032	0.017	0.027	1.86
	1980	8574	97.9	ND	0.115	0.032	0.017	0.027	1.90

[a] ND = not detectable.

Source: Evans et al. (1983)

1979 to 0.040 ± 0.011 ppm at the Custer NF site in 1977. The arithmetic mean concentration across all years and all three sites was 0.033 ppm. Fluctuations in the observed concentrations from year-to-year and site-to-site are demonstrated by the range of concentrations measured and by the size of the standard deviations as well. The lowest concentrations seen were below the limits of detection of the chemiluminescence monitor employed, but the highest concentrations observed at the Kisatchie NF and Green Mt. NF sites were both above the present ozone standard of 0.12 ppm. In 1979, only one excursion over 0.12 ppm O_3 was recorded at an NAPBN site. That excursion was recorded at the Mark Twain NF site in Missouri (Evans et al., 1983; Lefohn, 1984). In 1980, seven 1-hour excursions over 0.12 ppm were reported for Croatan NF, North Carolina (Lefohn, 1984). None of the NAPBN sites recorded an ozone concentration greater than 0.12 ppm in 1981 (Evans et al., 1983).

These summary statistics show somewhat higher mean concentrations, lower maximum concentrations, and lower standard deviations in data obtained at the Custer NF site than at the other two, which may indicate that meteorological conditions are less variable at that site or that the site is much less affected, if not altogether unaffected, by manmade ozone or its precursors.

During a 6-day period in 1979, the NAPBN site in the Mark Twain NF, Missouri, showed ozone concentrations well in excess of typical values. Table 5-3 shows the peak 1-hour value for each of the 6 days. A 1-hour value of 0.125 ppm, the maximum observed at any NAPBN site in 1979, was measured at that site on July 21, 1979. Evans et al. (1983) calculated the trajectories of air masses reaching the site during the 6-day period of July 18 through July 23, 1979. They ascribed the unusually high values, including the peak value on the 21st, to pollutants picked up as the trajectory passed over urban areas in the Ohio River Valley and the Great Lakes region. Figure 5-7 shows the trajectories for the air parcels reaching the Mark Twain NF site at midnight (0000), 8 a.m. (0800), noon (1200), and 6 p.m. (1800) on July 21, 1979. On July 23, clouds and rain spread over the region and the airflow trajectories shifted to the east and south, reducing both the quantities of transported precursors and the potential for photochemical ozone generation.

More recent and more comprehensive data from the NAPBN sites are presented in Table 5-4 and in Figures 5-8A and 5-8B. Table 5-4 presents the percentile distributions of ozone concentrations at all eight of the sites, aggregated by quarter across several years.

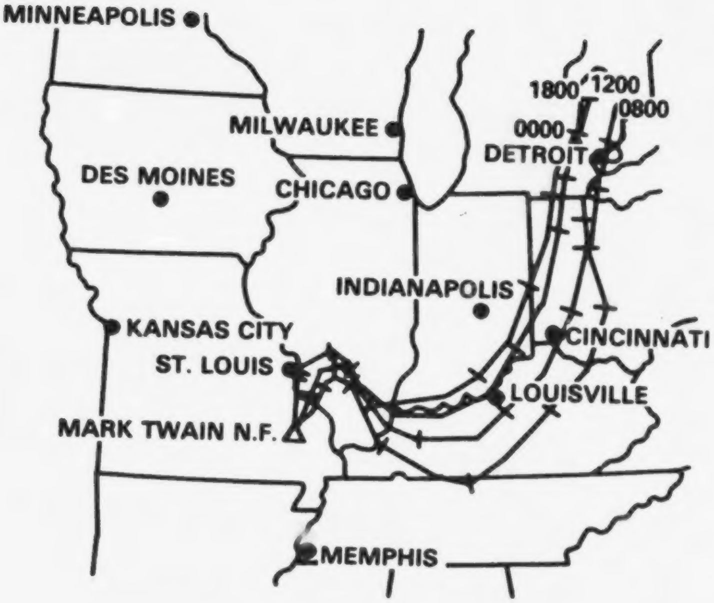
TABLE 5-3. CONCENTRATIONS OF OZONE DURING 6-day PERIOD OF HIGH VALUES AT NAPBN SITE IN MARK TWAIN NATIONAL FOREST, MISSOURI, 1979

Date	1-hr maximum O_3 concentration, ppm
July 18	0.080
July 19	0.100
July 20	0.115
July 21	0.125
July 22	0.120
July 23	0.050

Source: Evans et al. (1983)

As the data in Table 5-4 show, the arithmetic mean concentrations of ozone, for the years of data averaged, are generally higher in the second quarter of the year (April, May, June) than at other times at the NAPBN sites. Although a few excursions of the 1-hour concentration above 0.12 ppm were recorded at some of these sites, as discussed above (Evans et al., 1983; Lefohn, 1984), the distribution given in Table 5-4 clearly indicates that 99 percent of the 1-hour ozone concentrations measured at these sites are well below the present ozone standard. This is true even at those sites thought to be influenced by transport of ozone (Green Mt. NF) or demonstrated to be influenced by transport (Mark Twain NF, Evans et al., 1983). As shown in Table 5-4, the highest 99th percentile value was 0.093 ppm, reached at both the Green Mt. NF, VT, site (second quarter) and the Mark Twain NF, MO, site (third quarter). The maximum 1-hour ozone concentrations at these sites ranged from 0.050 ppm at Custer NF, MT (in the fourth quarter) to 0.155 ppm at Mark Twain NF, MO (in the third quarter). The second-highest 1-hour concentration among maximum daily 1-hour values ranged from 0.050 ppm at Custer NF, MT (fourth quarter) to 0.150 ppm at Mark Twain NF, MO (third quarter).

Five of the NAPBN monitoring stations (Apache NF, AZ; Mark Twain NF, MO; Custer NF, MT; Croatan NF, NC; Ochoco NF, OR) reported sufficient data for 1979 through 1983 to support an examination of their second-highest 1-hour


MINNEAPOLIS
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DETROIT
INDIANAPOLIS
KANSAS CITY
CINCINNATI
ST. LOUIS
LOUISVILLE
MARK TWAIN N.F.
MEMPHIS

Figure 5-7. Trajectory analysis plots for the NAPBN site at Mark Twain National Forest, MO, July 21, 1979 (distance between bars represents 12 hr).

Source: Evans et al. (1983).

TABLE 5-4. PERCENTILE DISTRIBUTIONS OF OZONE CONCENTRATIONS AT SITES OF NATIONAL AIR POLLUTION BACKGROUND NETWORK,[a] AGGREGATED BY QUARTER ACROSS SEVERAL YEARS (ppb)

Site, yr, and qtr	No. 1-hr meas.	Percentile						2nd highest 1-hr	Max 1-hr	Arith. mean
		10%	50%	80%	90%	95%	99%			
Apache, AZ (1980-1983)										
1	7587	32	39	45	49	50	54	65	75	39.3
2	7971	40	50	56	59	64	68	90	90	49.4
3	8407	28	40	46	51	54	60	85	90	39.5
4	8537	27	35	39	40	44	46	55	55	34.2
Kisatchie, LA (1977-1980, 1982)										
1	7093	16	32	43	53	60	73	120	125	32.4
2	6333	14	37	55	65	72	85	115	135	38.7
3	5462	6	22	42	53	60	70	110	110	25.8
4	6872	8	22	37	48	56	77	90	105	25.7
Mark Twain, MO (1979-1983)										
1	9484	14	32	41	47	52	63	80	85	31.0
2	10294	29	46	60	68	73	85	115	115	47.4
3	9155	23	42	55	65	75	93	150	155	43.2
4	8624	11	27	38	46	57	72	85	100	28.6
Custer, MT (1979-1983)										
1	6675	22	31	37	40	43	50	65	65	30.9
2	8646	30	40	46	50	53	59	80	80	40.3
3	8751	27	39	47	50	53	58	85	85	38.6
4	9956	18	28	32	35	36	40	50	50	26.9
Croatan, NC (1978-1983)										
1	10640	10	26	37	44	50	61	85	95	27.4
2	11491	12	36	51	60	66	79	110	150	36.1
3	8389	5	23	43	53	60	72	80	95	27.0
4	12036	4	18	29	37	41	54	85	85	19.8

TABLE 5-4 (continued). PERCENTILE DISTRIBUTIONS OF OZONE CONCENTRATIONS AT SITES OF NATIONAL AIR POLLUTION BACKGROUND NETWORK,[a] AGGREGATED BY QUARTER ACROSS SEVERAL YEARS (ppb)

Site, yr, and qtr	No. 1-hr meas.	Percentile						2nd highest 1-hr	Max 1-hr	Arith. mean
		10%	50%	80%	90%	95%	99%			
Ochoco, OR (1980-1983)										
1	7236	26	35	37	40	42	43	55	55	33.0
2	7861	28	38	45	46	51	54	60	75	37.1
3	8041	26	38	46	49	53	59	75	80	37.8
4	7467	22	31	32	36	39	41	55	60	29.2
Green Mt., VT (1977-1981)										
1	7387	21	31	41	45	48	61	120	135	32.8
2	7752	17	43	58	69	81	93	140	145	42.2
3	8636	5	26	44	56	65	86	110	115	29.2
4	8712	11	25	33	37	41	54	75	85	24.8
Chequamegon, WI (1979-1981)										
1	5548	22	36	45	51	56	65	80	80	36.1
2	6085	32	45	58	68	75	88	110	115	48.3
3	4577	15	30	45	53	58	75	90	95	33.0
4	5909	15	25	30	32	35	43	55	60	23.7

[a] Data are weighted by the number of 1-hr concentrations measured. Since data records were inadequate for some sites for some years, the years of data presented differ from site to site. The percentile distributions were derived from all 1-hr values for each quarter and all years listed. The maximum 1-hr and second-highest 1-hr concentrations represent the single value for each out of the entire data record for respective sites.

[b] These are the two highest values in the "daily maximum 1-hour" data set.

Source: Derived from Evans (1985).

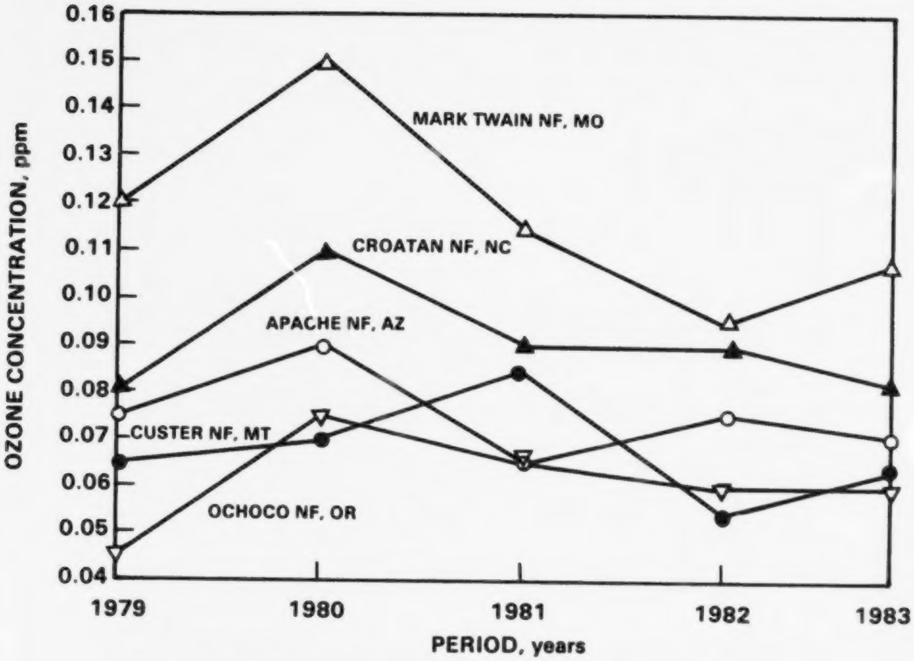


Figure 5-8A. Second-highest value among maximum 1-hr ozone concentrations at five NAPBN monitoring stations, 1979 through 1983.

Source: Derived from SAROAD (1985 b-f).

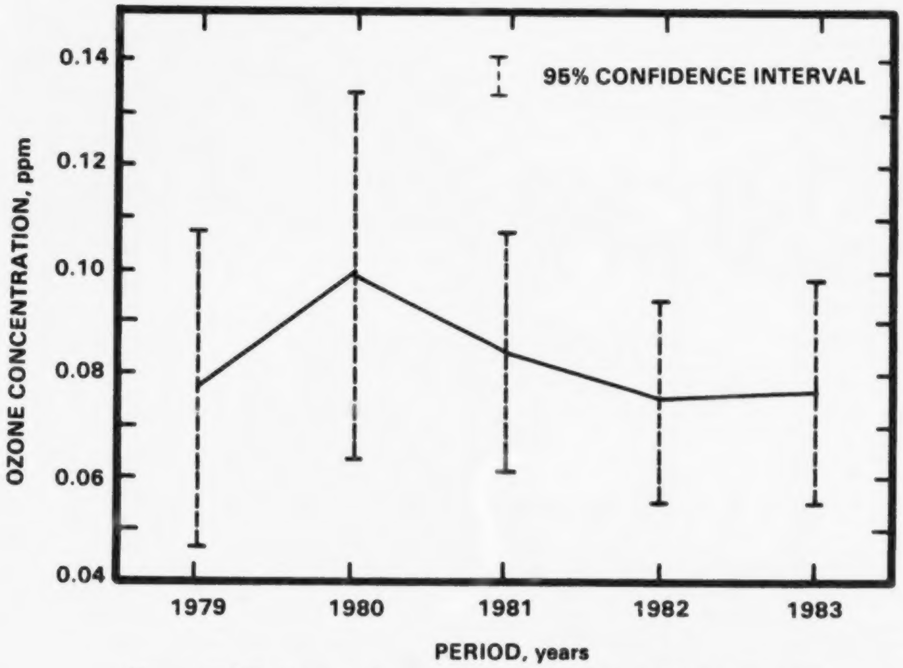


Figure 5-8B. Composite averages of the second-highest value among daily maximum 1-hr ozone concentrations at five NAPBN stations, 1979 through 1983.

Source: Derived from SAROAD (1985 b-f).

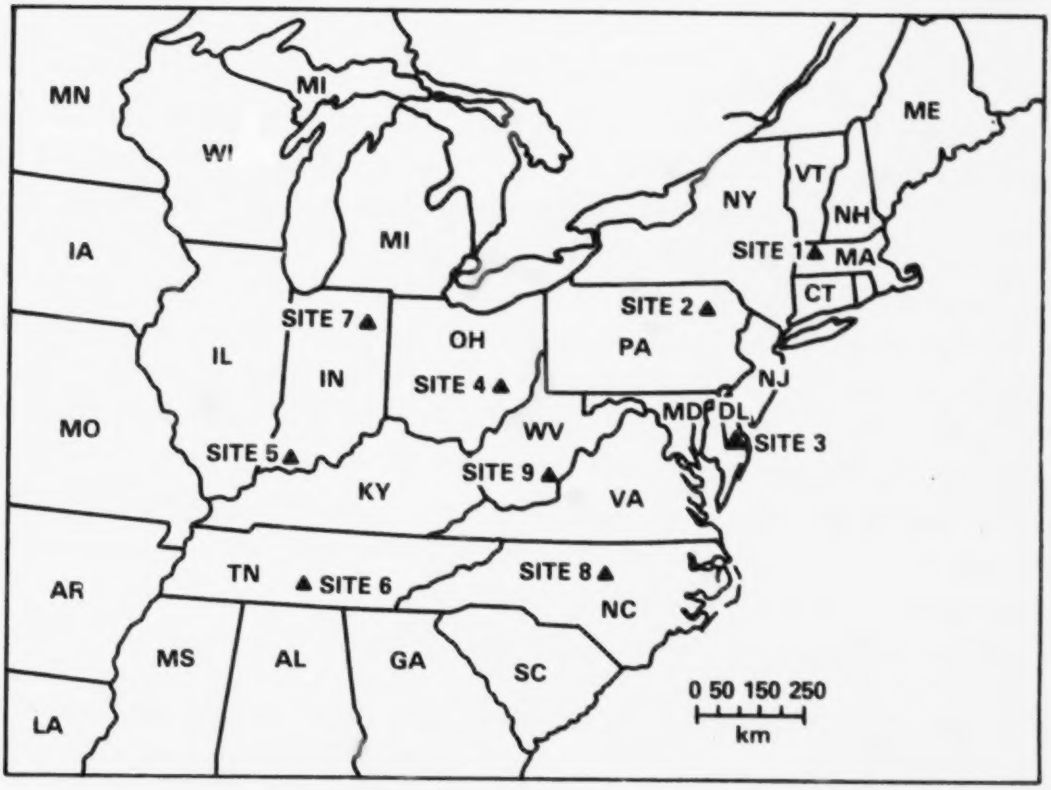
ozone values for evidence of trends. As seen in Figure 5-8B, however, the diversity of the NAPBN site characteristics, the consequent large variation in recorded values, and the small sample size result in such a large confidence interval around the average for each year that no trend can be determined. The data presented in Figures 5-8A and 5-8B show the NAPBN second-highest daily maximum 1-hour ozone concentrations to be about one-half those reported for urban-suburban sites for the same period (Figure 5-1).

5.4.2 Sulfate Regional Experiment Sites (SURE)

As part of a comprehensive air monitoring project sponsored by the Electric Power Research Institute (Martinez and Singh, 1979), ozone measurements were made by the chemiluminescence method in the last 6 months of 1977 at nine "nonurban" SURE sites in the eastern United States, shown in Figure 5-9. On the basis of diurnal NO_x patterns that indicated the influence of traffic emissions, five of the sites were classed as "suburban"; the other four were classed as "rural." The ozone data from these nine stations are summarized in Table 5-5. Martinez and Singh (1979) noted that the four rural stations occasionally recorded high values comparable with those in urban areas, but that the incidence was low. They concluded that infrequent transport of ozone or its precursors, or both, rather than local ozone generation, was the most probable cause of these high values.

5.5 VARIATIONS IN OZONE CONCENTRATIONS: DATA FROM SELECTED URBAN AND NONURBAN SITES

Variations of ozone concentrations by season and by time of day have been long known and are well documented. First studied in smog chambers, diurnal patterns have since been corroborated by field investigations, and exceptions to such general patterns have been examined and documented. Likewise, field investigations have substantiated general seasonal patterns and exceptions to them, and have also established a number of spatial variations in concentration, such as those that occur with latitude or with altitude. While it is difficult to discuss temporal and spatial variations separately, this section is subdivided along those lines for convenience.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SITE 2
SITE 3
SITE 4
SITE 5
SITE 6
SITE 7
SITE 8
SITE 9
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km

Figure 5-9. Location of Sulfate Regional Experiment (SURE) monitoring stations.

Source: Martinez and Singh (1979).

TABLE 5-5. SUMMARY OF OZONE CONCENTRATIONS MEASURED AT SULFATE REGIONAL EXPERIMENT (SURE) NONURBAN STATIONS, AUGUST THROUGH DECEMBER 1977

	Total no. of measurements	Number of measurements with concentrations:			Mean concn,. ppm	Mean of daily 1-hour maxima, ppm	1-hour maximum, ppm
		>0.08 ppm	>0.10 ppm	>0.12 ppm			
Rural sites							
#1 Montague, MA	3419	60	33	21	0.021	0.044	0.153
#4 Duncan Falls, OH	3441	52	2	0	0.029	0.049	0.107
#6 Giles Co., TN	3632	63	5	0	0.026	0.052	0.117
#9 Lewisburg, WV	3459	23	3	0	0.035	0.054	0.106
Suburban sites							
#2 Scranton, PA	3410	0	0	0	0.023	0.035	0.077
#3 Indian River, DE	3017	29	0	0	0.030	0.049	0.099
#5 Rockport, IN	3462	29	0	0	0.025	0.046	0.099
#7 Ft. Wayne, IN	3438	0	0	0	0.020	0.039	0.080
#8 Research Triangle Park, NC	3495	80	10	0	0.025	0.050	0.118

Source: Martinez and Singh (1979).

5.5.1 Temporal Variations in Ozone Concentrations

5.5.1.1 Diurnal Variations in Ozone Concentrations. By definition, diurnal variations are those that occur during a 24-hour period. Diurnal patterns of ozone may be expected to vary with location, depending on the balance among the many factors affecting ozone formation, transport, and destruction, as described in Chapter 3 and noted in Section 5.1. Although they vary with locality, diurnal patterns for ozone typically show a rise in concentration from low or near-zero levels to an early afternoon peak. The 1978 criteria document ascribed the diurnal pattern of concentrations to three simultaneous processes: (1) downward transport of ozone from layers aloft; (2) destruction of ozone through contact with surfaces and through reaction with nitric oxide (NO) at ground level; and (3) *in situ* photochemical production of ozone (U.S. Environmental Protection Agency, 1978; Coffey et al., 1977; Mohnen, 1977; Reiter, 1977a). Figure 5-10 shows the diurnal pattern of ozone concentrations on July 13, 1979, in Philadelphia, Pennsylvania. On this day a peak 1-hour average concentration of 0.20 ppm, the highest for the month, was reached at 2:00 p.m., presumably as the result of meteorological factors, such as atmospheric mixing, and local photochemical processes. The severe depression of concentrations to below detection limits (less than 10 ppb) between 3:00 and 6:00 a.m. is usually explained as resulting from the scavenging of ozone by local nitric oxide emissions. In this regard, this station is typical of most urban locations.

Diurnal profiles of ozone concentrations can vary from day to day at a specific site, however, because of changes in the various factors that influence concentrations. Such day-to-day variations are clearly demonstrated in Figure 5-11 (SAROAD, 1985c), which shows diurnal variations in ozone concentrations on 2 consecutive days at the same monitoring site in Detroit, Michigan. Differences in timing and magnitude occur that are especially noticeable between midnight and about 7:00 a.m. Transport is probably involved in these nighttime variations. The afternoon peak concentrations, the actual maxima for the 2 days, differ in magnitude but not in timing.

Composite diurnal data, that is, concentrations for each hour of the day averaged over multiple days or months, often differ markedly from the diurnal cycle shown by concentrations for a specific day. In Figures 5-12 through 5-14 (SAROAD, 1985d), diurnal data for 2 consecutive days are compared with composite diurnal data (1-month averages of hour-by-hour measurements) at three different kinds of sites: center city (Washington, DC), rural but near

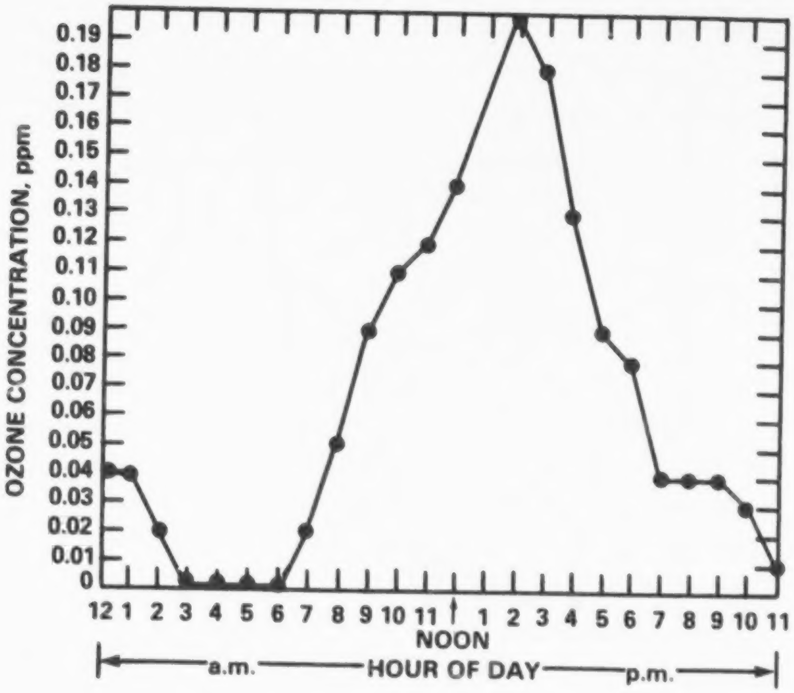

Figure 5-10. Diurnal pattern of 1-hr ozone concentrations on July 13, 1979, Philadelphia, PA.

Source: SAROAD (1985b).

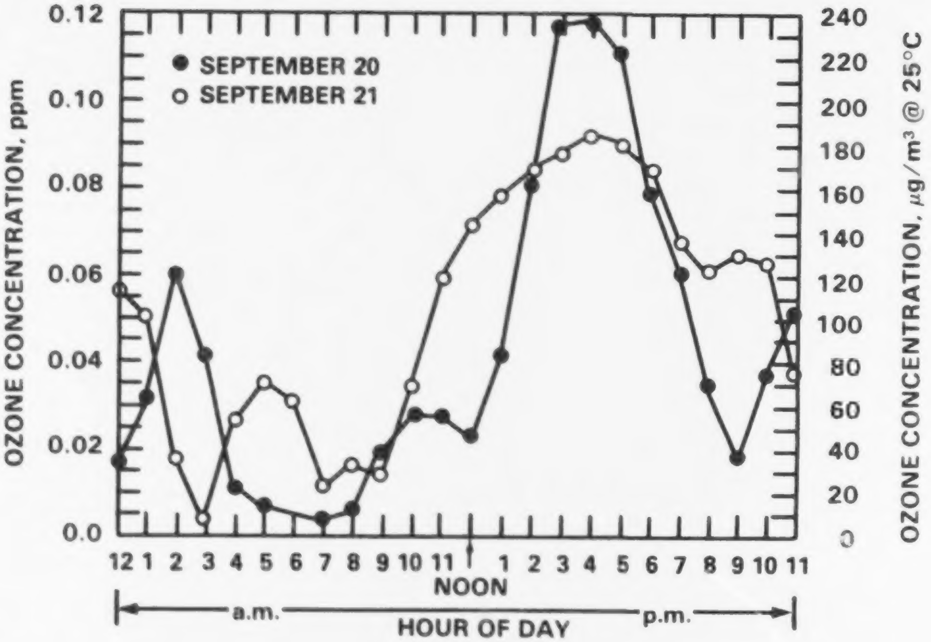

Figure 5-11. Diurnal patterns of 1-hr ozone concentrations, September 20 and 21, 1980, Detroit, MI.

Source: SAROAD (1985c).

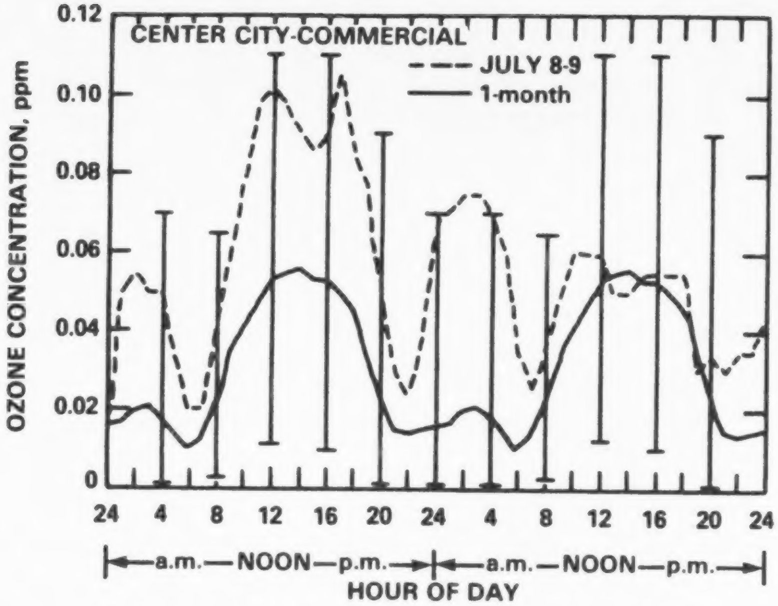

Figure 5-12. Diurnal and 1-month composite diurnal variations in ozone concentrations, Washington, DC, July 1981.
Source: SAROAD (1985d).

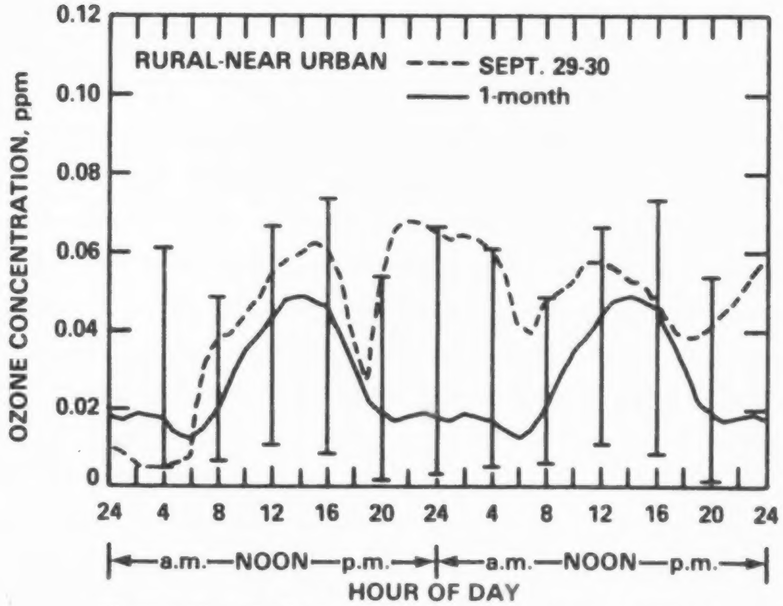

Figure 5-13. Diurnal and 1-month composite diurnal variations in ozone concentrations, St. Louis County, MO, September 1981.
Source: SAROAD (1985d).

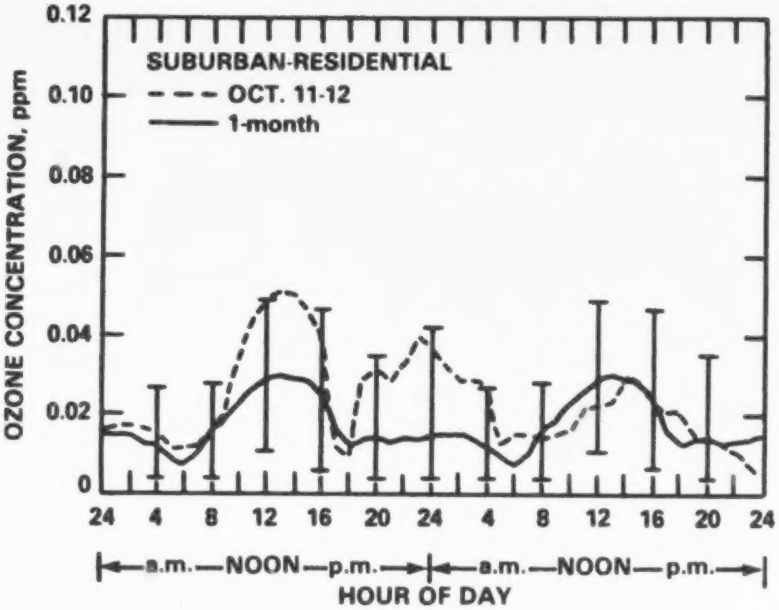

Figure 5-14. Diurnal and 1-month composite diurnal variations in ozone concentrations, Alton, IL, October 1981 (fourth quarter).

Source: SAROAD (1985d).

an urban area (St. Louis County, MO), and suburban-residential but in a crop-growing area (Alton, IL). Several obvious points of interest present themselves in these graphs: (1) at some sites, at least, peaks can occur at virtually any hour of the day or night but these peaks may not show up strongly in the longer-term average data; (2) some sites may be exposed to multiple peaks during a 24-hour period; and (3) disparities, some of them large, can exist between peaks (the diurnal data) and the 1-month mean (the composite diurnal data) of hourly ozone concentrations. These figures are given simply as examples of the differences that can occur between daily and monthly mean concentration patterns.

The effects of averaging are readily apparent when diurnal or short-term composite diurnal ozone concentrations are compared with longer-term composite diurnal ozone concentrations. When compared with Figures 5-12 through 5-14 (daily values and 1-month averages), Figure 5-15 (SAROAD, 1985d), based on 3-month averages, demonstrates rather graphically the effects of lengthening the period of time over which values are averaged. This figure shows a composite diurnal pattern calculated on the basis of 3 months. While seasonal

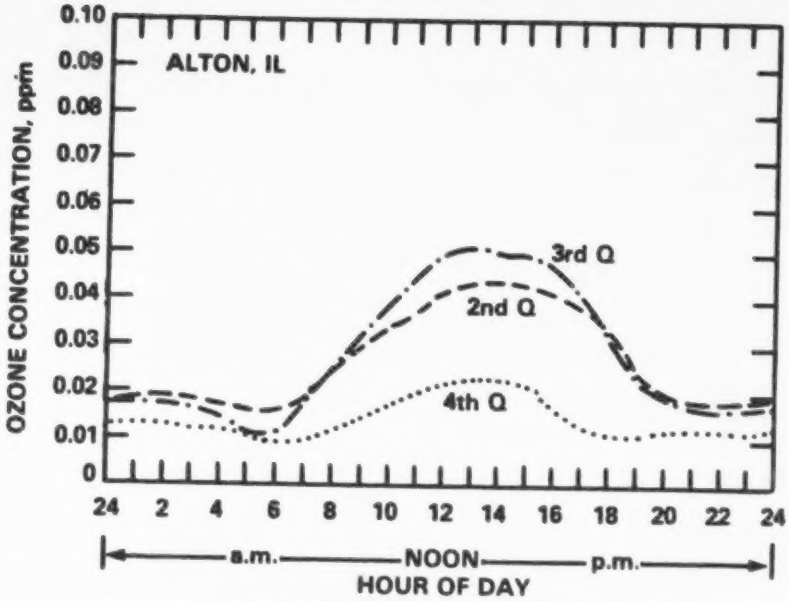

Figure 5-15. Composite diurnal patterns by quarter of ozone concentrations, Alton, IL, 1981.

Source: SAROAD (1985d).

differences are seen, and will be discussed later, the comparison of 3-month and 1-month composite diurnal concentrations at the Alton, IL, site readily demonstrates the smoothing out of peak concentrations as the averaging period is lengthened. Thus, a fourth pertinent point of interest, related to the third point cited above, emerges from the data presented above: that is, increasing the averaging time obscures the magnitude and time of occurrence of peak ozone concentrations. This is an obvious and familiar result in the statistical treatment of monitoring data, but one that is highly pertinent to the protection of human health and welfare from the effects of ozone.

The significance of the relationships of peak and mean concentrations depends upon whether the health and welfare effects of exposure to ozone are solely concentration-dependent, heavily concentration-dependent, or both concentration- and time-dependent. Depending upon whether acute or chronic exposures elicit the health and welfare effects of concern, careful attention may have to be paid to the relationship of short-term (e.g., 1-hour) versus longer averaging times.

Quantitative analyses of the relationships among maximum or second-highest 1-hour concentrations and daylight, diurnal, monthly, seasonal, and yearly average ozone concentrations lie outside the scope of this document. An example of one study, however, serves to describe the kinds of analyses that may be done to determine relationships among various exposure statistics or "averaging times." Lefohn and Benedict (1985) have examined the relationship between 7-hour and 12-hour (daylight) mean ozone concentrations averaged over a season (7 months). They also examined the relationships between each of these two exposure statistics and the 1-hour values during the same season $\geq$0.10 ppm. For their analyses they evaluated data records from all sites in the SAROAD network that met the following criteria: (1) existence of 4 years of monitoring data (1978 through 1981); (2) >4300 1-hour concentrations reported; and (3) the occurrence of exposures $\geq$10.2 ppm-hours, which was an index of sites exposed repeatedly to ozone concentrations $\geq$0.10 ppm over the specified time period. Sites so selected were then subjected to additional criteria that resulted in the identification of monitoring sites located in areas where agriculturally important cash crops were grown.

On the basis of calculated integrated exposures (hours times 1-hour concentrations $\geq$0.10 ppm), the monitoring sites thus identified were subdivided by Lefohn and Benedict (1985) into two categories: (1) those with 80 to 200 occurrences of 1-hour values $\leq$0.10 ppm (i.e., 80 to 200 hours at $\geq$0.10 ppm ozone), and (2) those with 200 to 1612 hours at $\geq$0.10 ppm O_3. To describe the quantitative relationships among the exposure statistics at sites in the two categories, a Pearson linear correlation matrix was calculated. For sites with 200 to 1612 occurrences of 1-hour concentrations $\geq$0.10 ppm, the correlation was 0.88 between the number of occurrences and the 7-hour seasonal mean and 0.93 between the number of occurrences and the 12-hour seasonal mean. The correlation between the 7- and 12-hour seasonal means was 0.96. When correlations were calculated from data obtained at sites with 80 to 200 occurrences of 1-hour concentrations $\geq$0.10 ppm, the correlations between occurrences and the 7- and 12-hour seasonal means were 0.40 and 0.47, respectively. The correlation for the two seasonal means at these sites was 0.94 (Lefohn and Benedict, 1985).

No attempt is made in this section to document the respective contributions of local formation of ozone versus transport of ozone; however, the occurrence of multiple peak ozone concentrations within a 24-hour period is usually construed as indicating the presence of ozone transported to the site from elsewhere. Figure 5-16 illustrates the diurnal variations that can be seen when transport occurs. Note the occurrence of dual peaks on each of 3 successive days at this site, part of the Sulfate Regional Experiment (SURE) network.

A familiar measure of ozone air quality is the number or percentage of days on which some specified concentration is equalled or exceeded. This measure, however, does not shed light on one of the more important questions regarding the effects of ozone on both people and plants; that is, the possible significance of high concentrations lasting 1 hour or longer and then recurring on 2 or more successive days.

In human controlled exposures, attenuation of responses to ozone has been observed at about 0.20 to 0.50 ppm in exercising subjects receiving repeated, consecutive-day exposures (see Chapter 10). That attenuation is lost after exposures to those levels cease (see Chapter 10 for the time course of loss of attenuation). It becomes of interest, therefore, to examine how many days in a row the maximum 1-hour ozone concentration reaches or exceeds specified levels in communities in high-ozone areas, as well as in other parts of the country.

The recurrence of high ozone concentrations on consecutive days was examined in data (SAROAD, 1985b-d) for one site in each of four cities: Pasadena and Pomona, CA; Washington, DC; and Dallas, TX. The numbers of multiple-day events were tallied by length of event (i.e., how many consecutive days) using data for the daylight hours (6:00 a.m. to 8:00 p.m.) in the second and third quarters of 1979 through 1981. These sites were chosen because they include areas known to experience high ozone concentrations (California), and because they represent different geographic regions of the country (west, southwest, and east). Similar data could be compiled for any city for which sufficient aerometric data exist. The choice of the 14-hour daylight period and of the second and third quarters is consistent with known diurnal and seasonal patterns of ozone concentrations and with typical human, crop, and ecosystem exposures.

In this discussion of the recurrence of respective specified ozone levels, a day or series of days on which the daily 1-hour maximum reached or exceeded

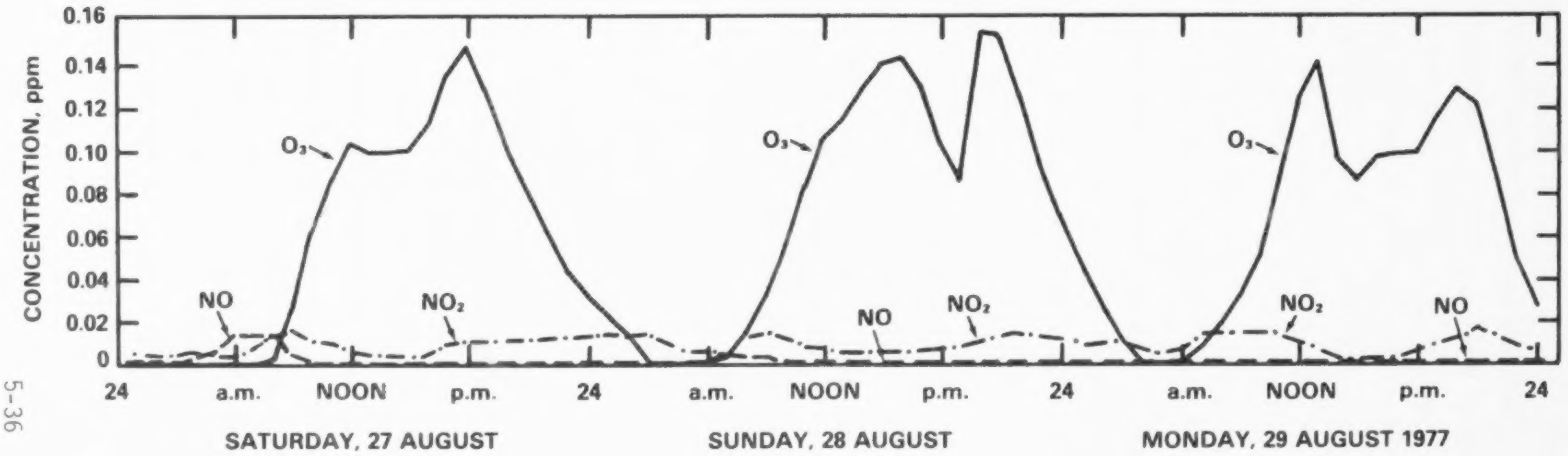

Figure 5-16. Three-day sequence of hourly ozone concentrations at Montague, MA, SURE station showing locally generated midday peaks and transported late peaks.

Source: Martinez and Singh (1979).

the specified level is called an "exposure"; the intervening day or days when that level was not reached is called a "respite." Four ozone concentrations were chosen: 0.06, 0.12, 0.18, and 0.24 ppm. The 1- to 7-day events (i.e., exposures or respites) are individually tabulated and events longer than 7 days are grouped together.

The summaries of "exposure" and "respite" events in Tables 5-6 through 5-9 show expected regional differences in the successive recurrence of these respective 1-hour concentrations. At the Dallas station, for example, the 3-year data tally shows 11 exposure events when the daily 1-hour maximum ozone value equalled or exceeded 0.06 ppm for more than 7 days in a row (Table 5-6). At first glance, the Pasadena station, with 10 such exposures, appears similar, but those 10 exposure events spanned 443 days; in Dallas the 11 exposures involved only 168 days. At this lowest concentration (≥ 0.06 ppm), the Dallas station recorded more short-duration (≤ 7 days) exposures (45) involving more days (159) than the Pasadena station (14 exposures over 45 days), simply because the daily 1-hour maximum statistic in Pasadena remained above 0.06 ppm for such protracted periods. At concentrations ≥ 0.12 ppm (Table 5-7), the lengthy exposures at the Pasadena site resolved into numerous shorter exposures; whereas in Dallas the exposures markedly dwindled in number and duration. At concentrations ≥ 0.18 ppm (Table 5-8), short-term (≤ 7 days) exposures in Pasadena were yet more numerous; Dallas had only two 1-day exposures. At ≥ 0.24 ppm (Table 5-9), the incidence rate of exposures at the Pasadena station finally decreased.

Note that these tables (Tables 5-6 through 5-9) also present the single and multiple-day periods when concentrations were lower than specified levels ("respites"); "event-days" include all "exposures" to and "respites" from specified concentrations, such that "total event-days" for a given site equal the total days monitored.

These tables give a more extensive indication of the long-term severity of ozone air quality at some of the selected sites than is given by the use of a 1-hour exposure statistic alone. The human responses to single acute exposures to ozone are well documented (Chapter 10), but the full significance of the attenuation of human responses to ozone over the course of a multiple-day exposure, and any possible consequences of the repetition of such multiple-day exposures within a smog season or over a number of years remain uncertain.

TABLE 5-6. NUMBER OF CONSECUTIVE-DAY EXPOSURES OR RESPITES WHEN THE DAILY 1-hr MAXIMUM OZONE CONCENTRATION WAS $\geq$ 0.06 ppm, IN FOUR CITIES (APRIL THROUGH SEPTEMBER, 1979 THROUGH 1981)

Length of event, days	"Exposures" ($\geq$0.06 ppm)				"Respites" ($\leq$0.06 ppm)			
	Pasadena	Pomona	Washington	Dallas	Pasadena	Pomona	Washington	Dallas
1	3	6	21	8	9	11	17	25
2	5	2	10	10	8	11	16	13
3	0	4	6	6	2	6	0	8
4	2	3	2	5	2	2	3	4
5	2	1	2	8	1	1	3	1
6	0	0	0	3	0	1	3	0
7	2	1	2	5	0	0	1	1
Subtotals								
Events	14	17	43	45	22	32	43	52
(Event-days)	(45)	(46)	(91)	(159)	(44)	(70)	(101)	(103)
>7	10	16	5	11	0	0	8	2
(Event-days)	(443)	(426)	(55)	(168)	(44)	(0)	(195)	(21)
Total events	24	33	48	56	22	32	51	54
(Total event-days)	(488)	(472)	(146)	(327)	(44)	(70)	(296)	(124)
Total days monitored	532	542	442	451	532	542	442	451

Source: SAROAD (1985b-d).

TABLE 5-7. NUMBER OF CONSECUTIVE-DAY EXPOSURES OR RESPITES WHEN THE DAILY 1-hr MAXIMUM OZONE CONCENTRATION WAS $\geq$ 0.12 ppm, IN FOUR CITIES (APRIL THROUGH SEPTEMBER, 1979 THROUGH 1981)

Length of event, days	"Exposures" ($\geq$0.12 ppm)				"Respites" ($\leq$0.12 ppm)			
	Pasadena	Pomona	Washington	Dallas	Pasadena	Pomona	Washington	Dallas
1	11	13	3	20	21	16	0	3
2	10	16	1	4	14	18	0	2
3	8	8	0	2	10	9	0	-
4	4	5	0	0	1	3	0	1
5	7	2	0	1	3	6	0	2
6	2	3	0	0	2	3	0	2
7	-	1	0	0	3	2	0	1
Subtotals								
Events	42	48	4	27	54	57	0	11
(Event-days)	(118)	(124)	(5)	(39)	(131)	(153)	0	(40)
>7	14	13	0	0	3	5	7	18
(Event-days)	(254)	(211)	(0)	(0)	(29)	(54)	(437)	(372)
Total events	56	61	4	27	57	62	7	29
(Total event-days)	(372)	(335)	(5)	(39)	(160)	(207)	(437)	(412)
Total days monitored:	532	542	442	451	532	542	442	451

Source: SAROAD (1985b-d).

TABLE 5-8. NUMBER OF CONSECUTIVE-DAY EXPOSURES OR RESPITES WHEN THE DAILY 1-hr MAXIMUM OZONE CONCENTRATION WAS $\geq$ 0.18 ppm, IN FOUR CITIES (APRIL THROUGH SEPTEMBER, 1979 THROUGH 1981)

Length of event, days	"Exposures" ($\geq$0.18 ppm)				"Respites" ($\leq$0.18 ppm)			
	Pasadena	Pomona	Washington	Dallas	Pasadena	Pomona	Washington	Dallas
1	21	24	0	2	15	15	0	0
2	9	12	0	0	8	11	0	0
3	10	9	0	0	14	9	0	0
4	6	4	0	0	3	4	0	0
5	3	4	0	0	7	5	0	0
6	4	4	0	0	2	1	0	0
7	1	2	0	0	3	2	0	0
Subtotals								
Events	54	59	0	2	52	47	0	0
(Event-days)	(139)	(149)	(0)	(2)	(153)	(125)	(0)	(0)
>7	7	2	0	0	11	16	3	5
(Event-days)	(90)	(20)	(0)	(0)	(150)	(248)	(442)	(449)
Total events	61	61	0	2	63	63	3	5
(Total event-days)	(229)	(169)	(0)	(2)	(303)	(373)	(442)	(449)
Total days monitored	532	542	442	451	532	542	442	451

Source: SAROAD (1985b-d).

TABLE 5-9. NUMBER OF CONSECUTIVE-DAY EXPOSURES OR RESPITES WHEN THE DAILY 1-hr MAXIMUM OZONE CONCENTRATION WAS $\geq$ 0.24 ppm, IN FOUR CITIES (APRIL THROUGH SEPTEMBER, 1979 THROUGH 1981)

Length of event, days	"Exposures" ($\geq$0.24 ppm)				"Respites" ($\leq$0.24 ppm)			
	Pasadena	Pomona	Washington	Dallas	Pasadena	Pomona	Washington	Dallas
1	20	21	0	0	7	8	0	0
2	13	10	0	0	1	4	0	0
3	5	0	0	0	6	5	0	0
4	2	2	0	0	4	2	0	0
5	2	1	0	0	3	2	0	0
6	0	0	0	0	1	1	0	0
7	0	0	0	0	0	1	0	0
Subtotals								
Events	42	34	0	0	22	23	0	0
(Event-days)	(79)	(54)	(0)	(0)	(64)	(62)	(0)	(0)
>7	1	1	0	0	23	14	3	3
(Event-days)	(9)	(9)	(0)	(0)	(380)	(417)	(442)	(449)
Total events	43	35	0	0	45	37	3	3
(Total event-days)	(88)	(63)	(0)	(0)	(444)	(479)	(442)	(449)
Total days monitored	532	542	442	449	532	542	442	449

Source: SAROAD (1985b-d).

5.5.1.2 Seasonal Variations in Ozone Concentrations. In addition to the diurnal cycles and between-day variations discussed in the preceding section, seasonal variations in ozone concentrations occur (for the reasons discussed in Chapter 3 and Section 5.1) and usually assume characteristic patterns.

In order to compile an assessment of potential ozone damage to the six leading commercial crops in the United States (corn, soybeans, hay, wheat, cotton, and tobacco), Lefohn (1982) surveyed 304 ozone monitoring stations and identified 24 that (1) were located in counties producing significant quantities of one or more of these six crops in 1978; (2) reported at least 50 percent of possible hourly data in 1978; (3) reported an hourly maximum of at least 0.1 ppm O_3; and (4) ranked high in cumulative ozone exposure for the period April to October 1978. Six of these sites represented counties with high soybean, wheat, or hay production. Quarterly composite diurnal patterns for six of these sites with reasonably complete ($\geq$75 percent) 1981 data are shown in Figure 5-17 (SAROAD, 1985d). The average levels are apparently comparable with the long-term averages at the NAPBN sites previously discussed (Section 5.4.1). In addition, the diurnal patterns for these sites clearly show the division of the afternoon ozone concentrations into two seasonal patterns, the low "winter" levels in the first and fourth quarters and the higher "summer" levels in the second and third quarters of the year.

Although averaging causes details to be obscured, the average diurnal patterns in Figure 5-17 show that the time of occurrence of peaks differs among sites, and, to an extent, between seasons. The seasonal differences in time of day are especially noticeable for the fourth quarter. Among the sites shown in Figure 5-17, ozone concentrations appear to peak at 2:00 to 2:30 p.m. in Little Rock in the higher-concentration second and third quarters. At Bakersfield in the second and third quarters, there is evidence, even from these composite data, of two peaks, the first at about 1:00 p.m. and the second at 5:00 to 6:00 p.m. At the Clark County, Ohio, site, the peak concentrations in the second and third quarters center around about 5:00 p.m., but they do not return to "baseline" until after midnight. The patterns at the Bakersfield and Clark County sites appear to indicate transport into the areas. It is also possible that single peaks that are shifted to mid- to late afternoon, as at the Little Rock site, are the product of transport. Depending upon proximity to urban centers and wind speed and direction, rural areas are typically exposed to their peak concentrations later than urban areas, usually within daylight hours but not always.

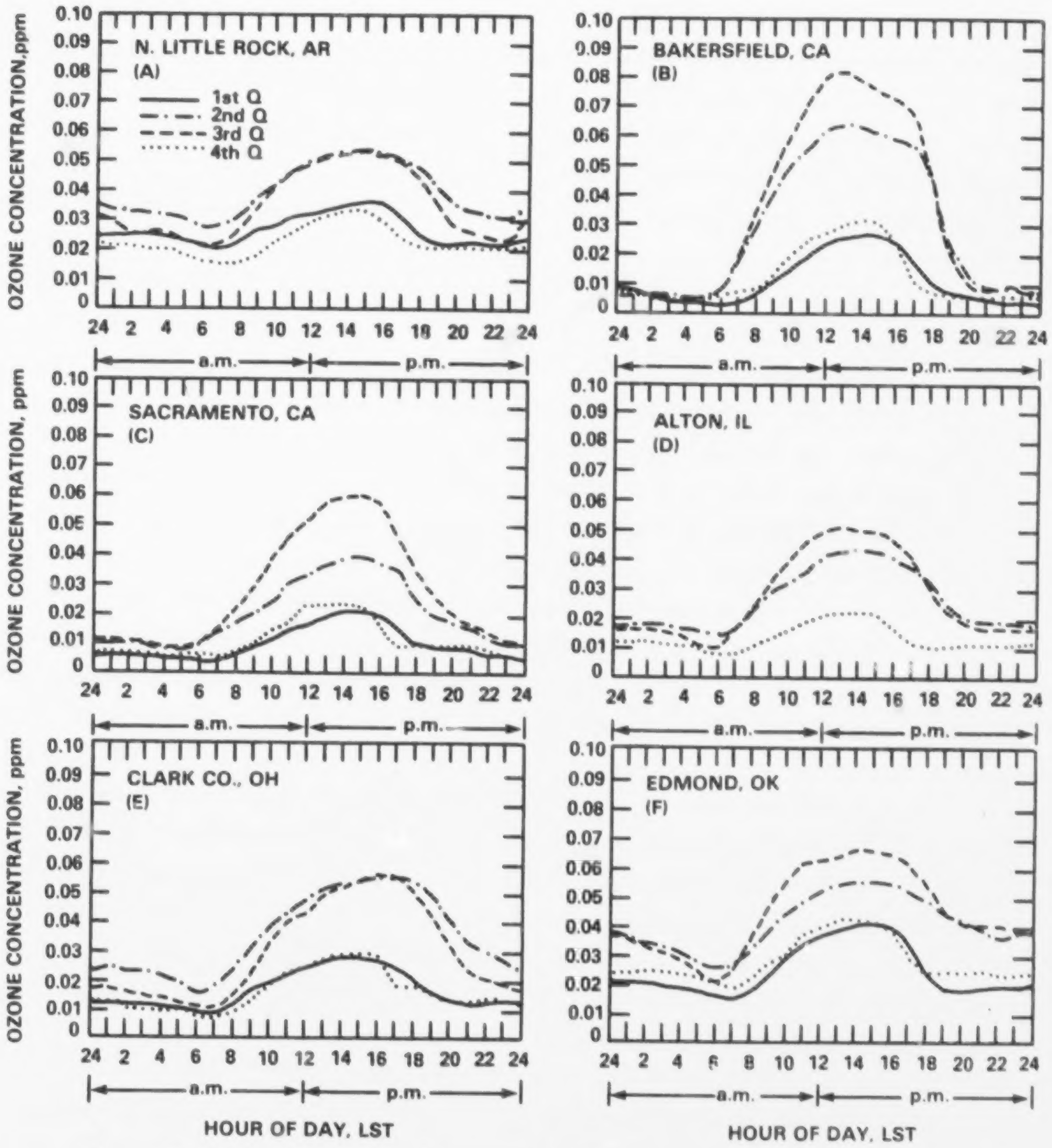

Figure 5-17. (A-F). Quarterly composite diurnal patterns of ozone concentrations at selected sites representing potential for exposure of major crops, 1981.

Source: SAROAD (1985d).

Composite diurnal variations in ozone concentrations at a rural site in Argonne, Illinois, over a 7-week period of the third quarter of 1980 are shown in Figure 5-18 (Kress and Miller, 1983). The actual day-to-day variations in ozone concentration over the entire third quarter of 1980 at that site are shown for comparison in Figure 5-19 (Kress and Miller, 1983). As part of the National Crop Loss Assessment Network, the site at Argonne monitors ozone concentrations over a 7-hour daytime period approximating the period of peak photosynthesis in crops. The data in Figure 5-18 yield a 24-hour average ozone concentration of 0.026 ppm (Kress and Miller, 1983). The 7-hour average for the same 7-week period at the Argonne site is 0.042 ppm (Kress and Miller, 1983). The day-to-day variations in both the 7-hour and the 24-hour averages (Figure 5-19) generally appear to be greater than the average difference within a day for either the 7-hour or 24-hour periods (Figure 5-18). The fluctuations in 1-hour values either within a day or from day to day, however, would be larger than within-day or between-day variations in either the 7-hour or the 24-hour average. The 7-hour average will be higher than the 24-hour average because the former excludes the low nighttime concentrations. As Figure 5-19 and its data illustrate, the selection of the appropriate averaging time is critical for the accurate description of dose-response relationships and for the protection of human, vegetation, and other receptors from the effects of ozone.

It is worth noting in this context that air pollution exposure statistics are of two basic functional types: descriptive and preventive. Descriptive exposure statistics simply define the conditions of concentration and exposure duration (averaging time) under which a specified effect has been observed or detected. Preventive exposure statistics are used prescriptively with the expectation of keeping a specified effect from happening. To be effective bases for an air quality standard, preventive exposure statistics must be (1) related to the true time-course of development of the specified effect(s), and (2) based on observed or predictable distributions, or both, of exposure conditions over the range of concentrations and durations producing the effect(s) of concern.

In Figure 5-20 (A-H), seasonal variations in ozone concentrations in 1981 are depicted using 1-month averages and the single 1-hour maximum concentration within the month for eight sites across the nation (SAROAD, 1985d). The data from most of these sites exhibit the expected pattern of high ozone

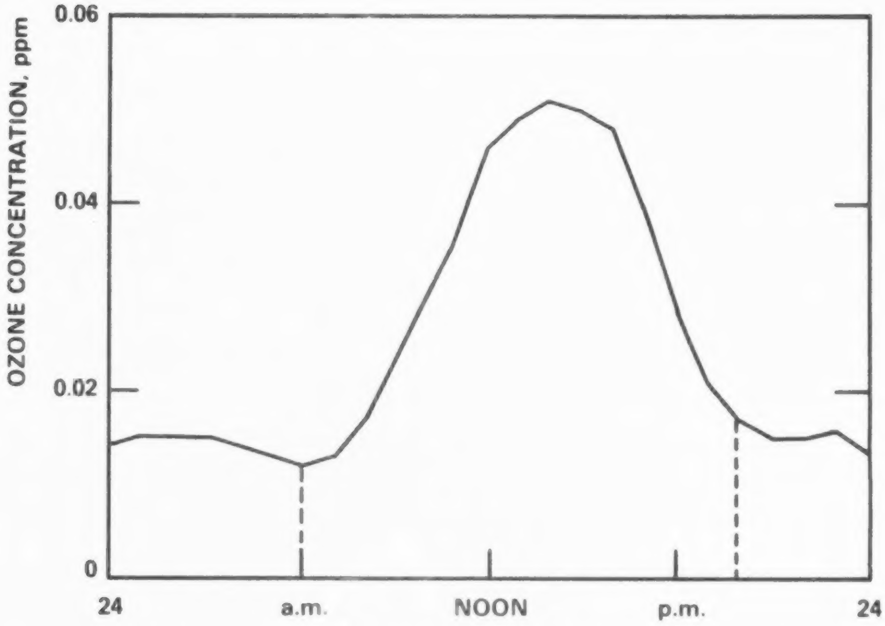

Figure 5-18. Composite diurnal ozone pattern at a rural NCLAN site in Argonne, IL, August 6 through September 30, 1980.
Source: Kress and Miller (1983).

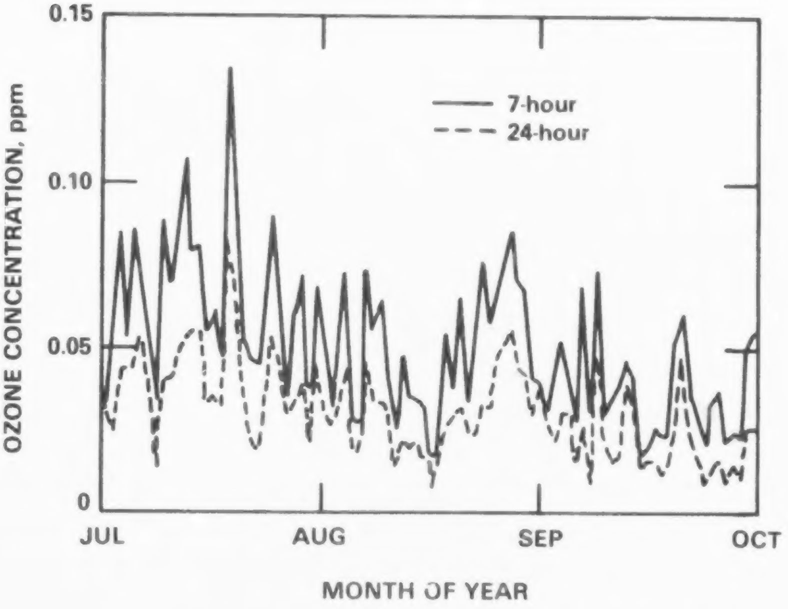

Figure 5-19. Daily 7-hour and 24-hour average ozone concentrations at a rural NCLAN site in Argonne, IL, 1980.
Source: Kress and Miller (1983).

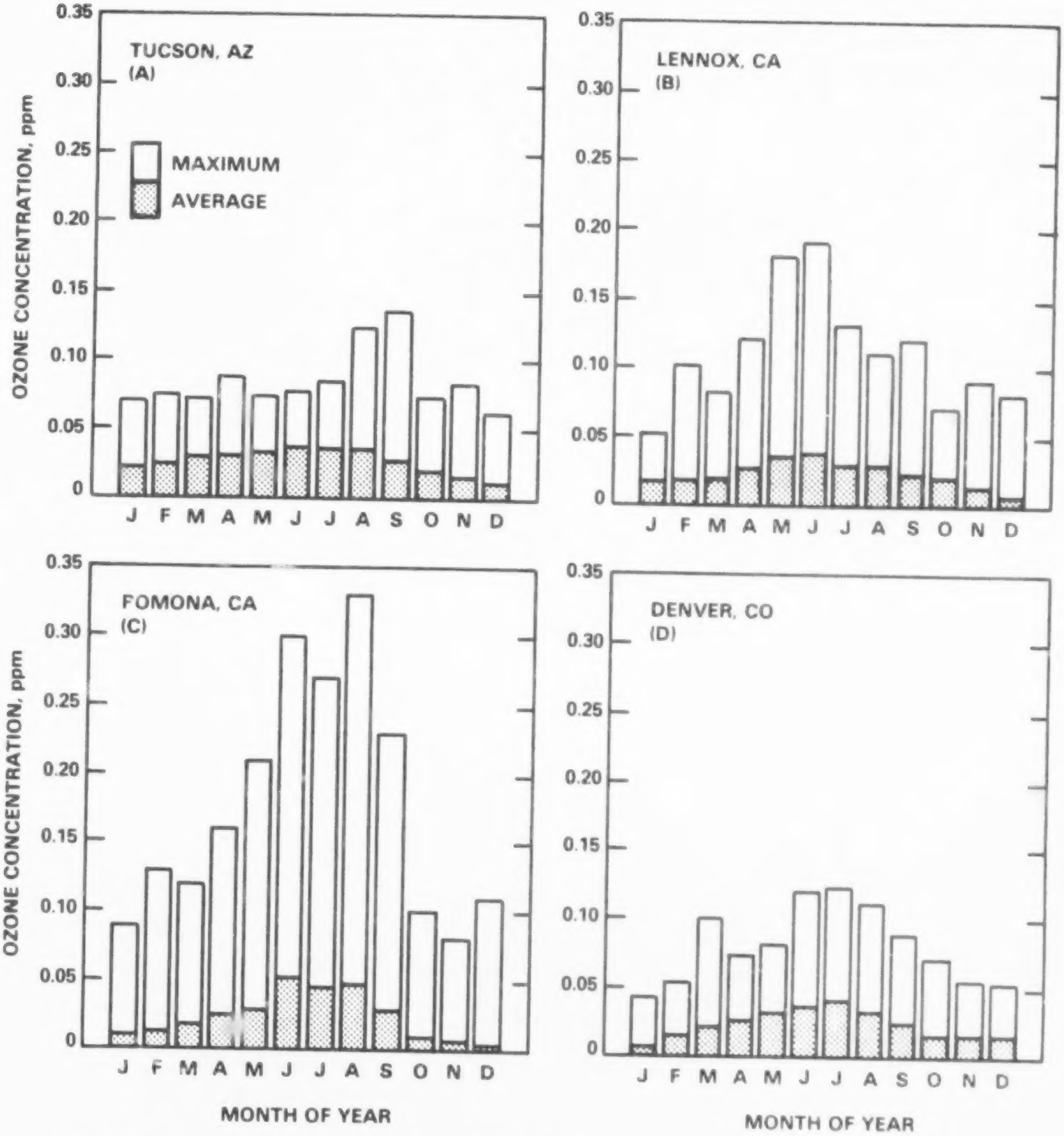

Figure 5-20. (A-H). Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-hour maximum in each month at selected sites, 1981.

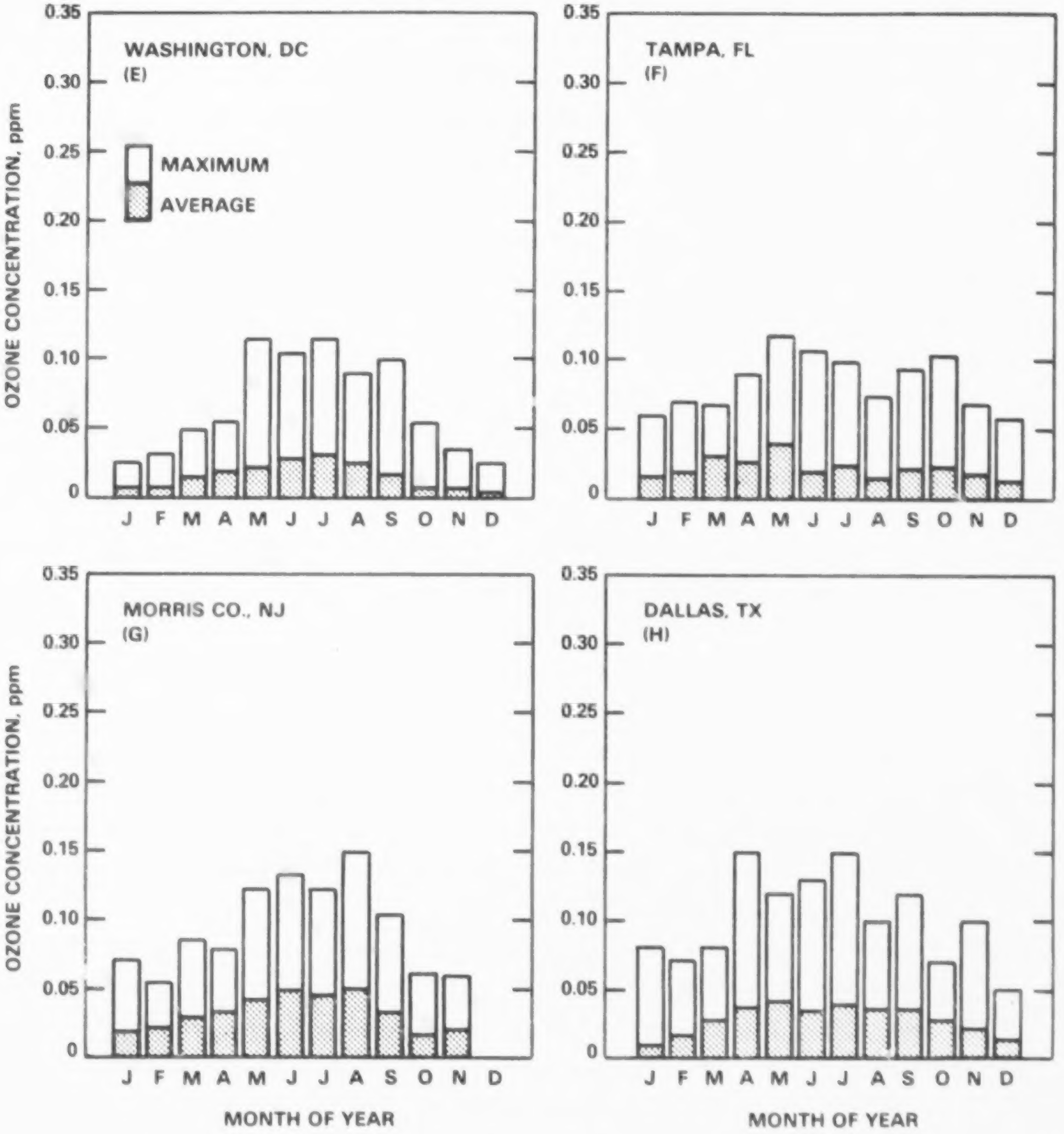

Figure 5-20. (A-H) (continued). Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-hour maximum in each month at selected sites, 1981.

Source: SAROAD (1985d).

levels in late spring or in summer and low levels in the winter. Data for Pomona (Figure 5-20C) and Denver (Figure 5-20D) show summer maxima. Tampa shows a late spring maximum but with concentrations in the fall (October) approaching those of spring (June) (Figure 5-20F). Dallas data also tend to be skewed toward higher spring concentrations; but note that November concentrations are also relatively high (Figure 5-20H). Averaging together data for several years would give a smoother "characteristic" pattern but also would obscure the fact that local, and even national, weather in a particular year plays at least as big a role in the formation of ozone as the regular seasonal changes in the elevation of the sun and the resulting variations in insolation. Because of seasonal changes in storm tracks from year to year, the general weather conditions in a given year may be more favorable for the formation of ozone and other oxidants than during the prior or following year. Thus, short-term concentration trends may not be indicative of real changes in air quality.

5.5.1.3 Weekday-Weekend Variations in Ozone Concentrations. Atmospheric ozone concentrations represent the combined effects of emission sources and meteorological conditions. The various sections of this chapter have been based on the assumption that ozone precursor sources operate on a generally steady-state or at least on an average, repeatable diurnal cycle. For the most part, urban source patterns of oxidant precursors do appear to be reasonably constant; however, in most urban areas changes occur in traffic and commercial emission patterns that are keyed to a weekday-weekend activity cycle. The effects of these changes have been observed in corresponding changes in ozone concentration patterns.

Debate in the 1960s over the role of nitric oxide (NO) in scavenging ozone led to the examination of whether weekday-weekend differences in ozone concentrations might occur in urban areas, on the assumption that NO emissions would be lower on weekends when some NO_x-emitting sources virtually shut down. Altshuller (1975) reported the observation that no alerts had ever occurred in the Los Angeles Basin on a Sunday. Likewise, Elkus and Wilson (1976), Levitt and Chock (1976), and Graedel et al. (1977) reported the existence of a weekday-weekend difference in ozone concentrations. While not reporting lower average ozone concentrations on weekends for the Los Angeles Basin, Schuck et al. (1966) noted a spatial shift of concentrations on summer weekends, away from the central commercial and urban areas to suburban and coastal areas. They attributed the spatial shift in concentrations to changes in traffic patterns resulting from a shift from job-related travel to recreational travel.

No newer reports of possible weekend-weekday variations are available in the literature, but any exhaustive exposure assessment should take into consideration the possibility that subtle differences in absolute concentrations or their spatial and temporal patterns could have some effect on total exposure.

5.5.2 Spatial Variations in Ozone Concentrations

Ozone is commonly thought of as a relatively homogeneous, regional pollutant, largely because of the nature of the sources of its precursors and the processes that contribute to its formation as a secondary pollutant. Numerous factors affect the occurrence of ozone in ambient air, however, so that differences in the true exposures sustained by respective receptors (e.g., human populations, crops, natural ecosystems) will vary within regions, airsheds, or other defined areas. The data presented in this section demonstrate a few of the known spatial variations in ozone concentrations that should be taken into account when assessing actual or even potential exposures. The data presented in this brief section are intended to be illustrative rather than exhaustive, since numerous meteorological, topographical, and physicochemical factors will influence the spatial and temporal distributions of ozone concentrations at specific sites.

5.5.2.1 Urban versus Nonurban Variations. Data were presented in the 1978 criteria document demonstrating that peak concentrations of ozone in rural areas are generally lower than those in urban areas, but that "dosages or average concentrations in rural areas are comparable to or even higher than those in urban areas" (U.S. Environmental Protection Agency, 1978). The diurnal concentration data presented in the preceding section indicate that peak ozone concentrations can occur later in the day in rural areas than in urban, with the distance downwind from urban centers generally determining how much later the peaks occur. The data presented in the preceding section for Montague, Massachusetts, in Figure 5-16 (Martinez and Singh, 1979) exemplify high late-afternoon secondary peak concentrations resulting from transport.

The NAPBN and other nonurban data presented in Section 5.4 illustrate the urban-nonurban gradient in ozone concentrations that generally exists, and support the statement quoted above from the 1978 document. While corroboration of that statement would require the calculation of means or ppm-hours, the data given in Section 5.4.2 tend to support that conclusion. For example, data presented in that section (Table 5-5) showed that rural sites of the SURE network were exposed, on the average, to daily maximum 1-hour ozone concentrations in excess of those to which the suburban sites were exposed (Martinez and Singh, 1979). While one rural site recorded 21 occurrences of 1-hour ozone concentrations >0.12 ppm during August through December 1977 (referred to below as A-D), the suburban sites recorded no such occurrences. All four of the rural sites in the SURE network recorded two or more occurrences (and one recorded 33 such occurrences) of daily maximum 1-hour concentrations >0.10 ppm; only one of the five suburban sites recorded the occurrence (n = 10) of that concentration over the same period (A-D). All exposure statistics examined by Martinez and Singh (1979) for the SURE concentration data were higher at the rural sites, on the average, than at the suburban sites. The respective statistics, weighted by the number of observations in the data record, were: average of 24-hour mean concentrations (A-D), 0.028 ppm at rural versus 0.024 ppm at suburban sites; mean of daily maximum 1-hour (A-D), 0.050 ppm at rural versus 0.044 ppm at suburban sites; and the 1-hour maximum for the whole period (A-D), 0.121 ppm at rural sites versus 0.094 ppm at suburban sites.

In another example, data reported by Lefohn (1984) from sites classified as rural in the SAROAD data bank showed 9 occurrences of daily maximum 1-hour ozone concentrations >0.12 ppm at a rural Preble County, Ohio, site; and 19 such occurrences at a rural site in Camden County, New Jersey.

In addition to the occurrence of higher mean concentrations and occasionally higher peak conccentrations in nonurban areas than in urban, it is well documented that ozone persists longer in nonurban than in urban areas (Coffey et al., 1977; Wolff et al., 1977; Isaksen et al., 1978). The absence of chemical scavengers appears to be the chief reason.

5.5.2.2 Intracity Variations. Despite relative intraregional homogeneity, evidence exists for intracity variations in concentrations that are pertinent to potential exposures of human populations and to the assessment of actual exposures sustained in epidemiologic studies. Two illustrative pieces of data are presented in this section, one a case of relative homogeneity in a city with a population under 500,000 (New Haven, Connecticut) and one a case of relative inhomogeneity of concentrations in a city of greater than 9 million population (New York City) (U.S. Department of Commerce, 1982).

New Haven, Connecticut, was the site of an epidemiological study in 1976 by Zagraniski et al. (1979). Symptoms recorded in diaries kept by study participants were correlated with ozone concentrations measured by the chemiluminescence method at a downtown New Haven site characterized as Center City-Residential. Table 5-10 shows several percentiles in the distribution of hourly values for that site plus two other monitoring stations in the county that were operating at the time, one in Derby, Connecticut, 9 miles west of New Haven, and one in Hamden, Connecticut, 6 miles north of New Haven. The Derby site also is characterized as Center City-Commercial, the Hamden site as Rural-Agricultural. The general similarity of values among the three sites appears to substantiate the New Haven data used in the epidemiological study since there was probably a reasonable temporal correlation between these close sites. Thus, wherever individuals might have traveled about the county, they probably were exposed to similar concentrations of ambient ozone. This conclusion is reinforced by the data in Table 5-11, showing the date and time of the maximum hourly concentrations by quarter at these three sites. The significant data are those for the second and third quarters when the potential for O_3 formation and for exposure was the greatest. Differences in peak concentrations varied from 0.006 ppm in the fourth quarter to 0.055 ppm in the third quarter among sites.

The source of much of the ozone found in the New Haven, Connecticut, area is the greater New York City area (e.g., Wolff et al., 1975; Cleveland et al., 1976a,b) and an urban plume transported over the distance from New York City to New Haven would tend to be relatively well-mixed and uniform, such that intracity variations in New Haven would probably be minimal.

The highest or second-highest 1-hour maximum ozone concentration reported from a given station during a given year frequently gives an indication of the potential for repeated human exposure to high ozone levels. Nevertheless, a one-to-one correspondence between peak levels and either the number of days or the number of hours that a given level may be exceeded does not necessarily exist. Data obtained in the metropolitan New York area in 1980 illustrate this latter fact (Smith, 1981); and illustrate, as well, that intracity gradients can exist that should be taken into account in exposure assessment. The data given in Table 5-12 were obtained at the monitoring sites shown in Figure 5-21. The second-highest 1-hour ozone readings at the Eisenhower Park and Queens College stations have values only a few percentage points apart,

TABLE 5-10. OZONE CONCENTRATIONS AT SITES IN AND AROUND NEW HAVEN, CONNECTICUT, 1976 (CHEMILUMINESCENCE METHOD, HOURLY VALUES IN ppm)

Site (SAROAD No.)	No. measurements	% of values ≤ stated concentration				Max concn.
		50%	90%	95%	99%	
New Haven, CT (070700123F01)	4119	0.021	0.035	0.091	0.162	0.274
Derby, CT (070190123F01)	5698	0.023	0.038	0.071	0.095	0.290
Hamden, CT (070400001F01)	3853	0.030	0.045	0.075	0.098	0.240

Source: SAROAD (1985a).

TABLE 5-11. QUARTERLY MAXIMUM 1-HOUR OZONE VALUES AT SITES IN AND AROUND NEW HAVEN, CONNECTICUT, 1976 (CHEMILUMINESCENCE METHOD, HOURLY VALUES IN ppm)

	Quarter of Year			
	1	2	3	4
New Haven, CT				
No. measurements	10	1964	2079	66
Max 1-hr, ppm	0.045	0.274	0.235	0.066
Hour of day	11:00 a.m.	2:00 p.m.	2:00 p.m.	10:00 p.m.
Date	3/29	6/24	8/12	10/3
Derby, CT				
No. measurements	11	2140	2187	1360
Max 1-hr, ppm	0.015	0.280	0.290	0.060
Hour of day	11:00 p.m.	2:00 p.m.	2:00 p.m.	7:00 p.m.
Date	3/31	6/24	8/12	12/20
Hamden, CT				
No. measurements	56	2065	1446	286
Max 1-hr, ppm	0.050	0.240	0.240	0.065
Hour of day	Noon	3:00 p.m.	1:00 p.m.	3:00 p.m.
Date	3/29	6/24	7/20	10/7

Source: SAROAD (1985a).

TABLE 5-12. PEAK OZONE CONCENTRATIONS AT EIGHT SITES IN NEW YORK CITY AND ADJACENT NASSAU COUNTY, 1980[a]

Site	Site no.	No. 1-hr averages >0.12 ppm	Days with 1-hr averages >0.12 ppm	Four highest 1-hr daily values, ppm, and date			
				1st	2nd	3rd	4th
Susan Wagner H.S.	1	20	8	0.174 (8/28)	0.152 (7/18)	0.140 (7/26)	0.131 (9/1)
Mabel Dean H.S.	2	19	10	0.155 (7/21)	0.154 (7/26)	0.144 (7/18)	0.139 (8/28)
Woolsey Post Office	3	37	6	0.188 (7/20)	0.163 (7/21)	0.151 (7/22)	0.148 (8/28)
Mamaroneck	4	0	0	0.092 (6/14)	0.080 (8/28)	0.076 (7/2)	0.075 (7/26)
P.S. 321	5	24	9	0.148 (7/26)	0.146 (8/28)	0.145 (7/18)	0.144 (7/9)
Sheepshead Bay H.S.	6	44	12	0.184 (7/31)	0.173 (7/18)	0.165 (8/7)	0.164 (7/14)
Queens College	7	51	15	0.174 (8/28)	0.164 (7/21)	0.163 (6/14)	0.159 (8/24)
Eisenhower Park	8	7	2	0.175 (8/28)	0.158 (7/21)	0.119 (7/20)	0.118 (8/24)

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[a] Sites monitored during the Northeast Corridor Monitoring Program (NECRMP); site numbers assigned here are keyed to Figure 5-21.

Source: Smith (1981).

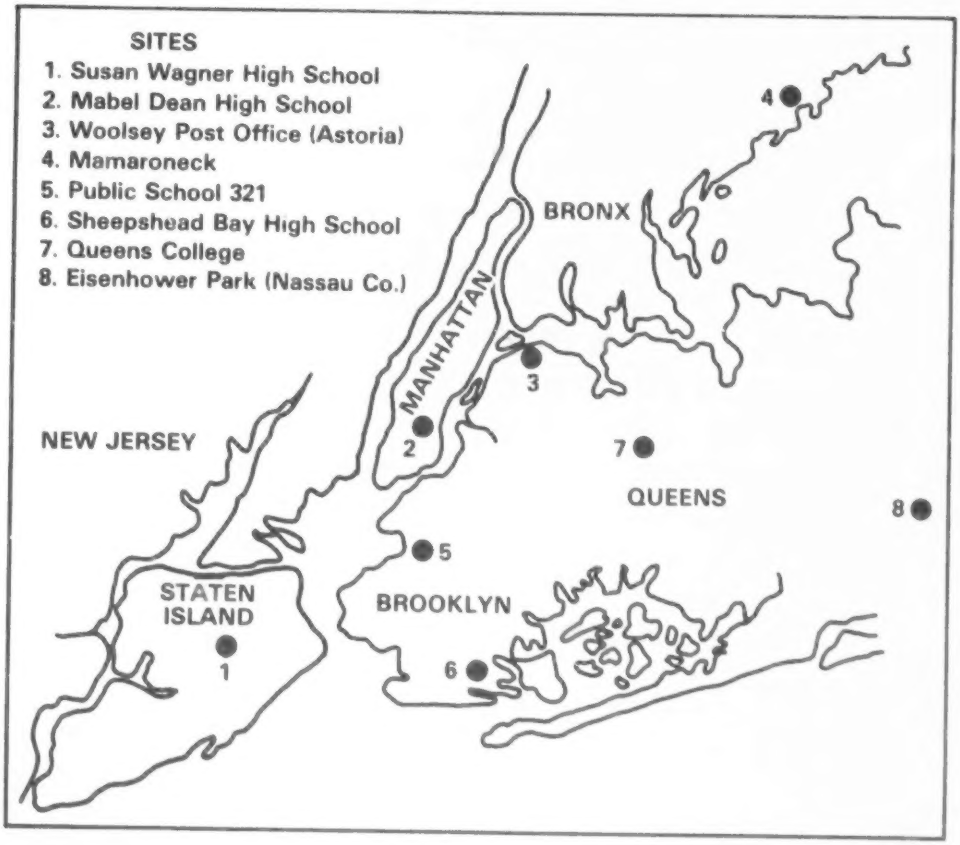
SITES
1. Susan Wagner High School
2. Mabel Dean High School
3. Woolsey Post Office (Astoria)
4. Mamaroneck
5. Public School 321
6. Sheepshead Bay High School
7. Queens College
8. Eisenhower Park (Nassau Co.)
BRONX
MANHATTAN
NEW JERSEY
QUEENS
STATEN ISLAND
BROOKLYN
1
2
3
4
5
6
7
8

Figure 5-21. New York State air monitoring sites for Northeast Corridor Monitoring Program (NECRMP).

Source: Smith (1981).

yet there were 51 hours of ozone concentrations exceeding 0.12 ppm and 15 days when ozone levels exceeded 0.12 for at least 1 hour at the Queens College Station; whereas corresponding values were recorded at Eisenhower Park for only 7 hours during 2 days. At both stations, data for about 94 percent of possible hours were recorded as valid.

The range of first-, second-, third-, and fourth-highest values, along with frequencies of values >0.12 ppm, establishes an apparent concentration gradient in the area from sites 6 and 5 to site 4. Exposures of human populations living and working in metropolitan New York City could differ appreciably if the residences were located and all activities were centered in lower Brooklyn as opposed to the upper Bronx. Differences in peak concentrations at the respective sites varied by date (6/14 to 8/28) and by level on the same day (8/28), when ozone was 0.080 ppm at site 4 and 0.174 at site 7, a difference of 0.094 ppm (a factor of 2.18).

Intracity gradients in ozone concentrations have also been reported by Kelly et al. (1986) for a 1981 study in Detroit, MI. Ozone concentrations were measured for about 3 months at 16 sites in the metropolitan Detroit area and in nearby Ontario, Canada. Values at 15 sites were correlated with those at a site adjacent to the Detroit Science Center, about 3 km north of the central business district in Detroit. In general, the correlation decreased as distance from the Science Center site increased; and, in general, the actual concentrations increased with distance from that site toward the north-northeast. The highest ozone concentrations were recorded at sites about 10 to 70 km north-northeast of the urban core. At greater distances or in other directions, ozone maxima decreased.

5.5.2.3 Indoor-Outdoor Concentration Ratios. Most people in the United States spend a large proportion of their time indoors. Although knowledge of actual exposures of populations to ozone is essential for optimal interpretation and use of the results of epidemiological studies, essentially all air pollution monitoring is done on outdoor air. The modeling of actual exposures, as opposed to potential exposures, therefore necessitates knowing general activity patterns and at least approximate indoor/outdoor ratios (I/O) of ozone.

For slowly reacting compounds such as carbon monoxide, long-term average ratios of indoor to outdoor concentrations tend to be close to unity, in the absence of indoor sources. Over short time periods, however, the I/O may be significantly different because of non-equilibrium factors (Yocom, 1982). The situation for reactive pollutants such as ozone is much more complex, and reported I/O values for ozone are highly variable. Unfortunately, the number of experiments and kinds of structures examined to date provide only limited data for use in modeling indoor exposures. Yocom (1982) has presented a chronological summary of studies in which either ozone or photochemical oxidant indoor-outdoor gradients in buildings and residences were measured. Studies summarized by Yocom have been conducted over the period 1971 through the present (one ongoing study) by five research organizations: University of California, the California Institute of Technology, GEOMET, Inc., Lawrence Berkeley Laboratory, and TRC Environmental Consultants. Structures examined have included hospitals, schools, office buildings, single-dwelling homes, "experimental" dwellings, apartments, and mobile homes. Private homes included those with and without gas stoves and fireplaces, and those inhabited by smokers versus nonsmokers. Areas of the country in which the buildings were located ranged from Southern California to Boston, including such cities in between as Denver, Chicago, Washington, Baltimore, Pittsburgh, as well as other unspecified locations (Yocom, 1982). The indoor-outdoor ratios reported from these studies are summarized in Table 5-13 and are discussed later.

Among newer reports of indoor/outdoor gradients in ozone concentrations, also summarized in Table 5-13, are the studies of Stock et al. (1983) and Contant et al. (1985), undertaken to provide exposure assessments for an epidemiological study of asthmatics in Houston, Texas, in 1981 (see Holguin et al., 1985, in Chapter 11). Stock et al. (1983) found I/O ratios of nearly zero to 0.09 in one air-conditioned residence (maximum ozone concentration of 5 ppb) and an I/O ratio of 1.0 in a residence ventilated completely by outdoor air. (Indoor concentrations were monitored via a sampling manifold connected by Teflon lines to a chemiluminescence analyzer in a mobile van parked near the respective houses.) Contant et al. (1985), in a continuation and extension of the same study, used "personal monitors" (i.e., portable analyzers) to measure indoor and outdoor air in the immediate environs of participants in the asthma study. Mean, median, and maximal ozone concentrations, respectively, were 10.8, 5, and 147 ppb indoors and 51.8, 42, and 250 ppb outdoors. The respective I/O ratios were 0.21, 0.12, and 0.59.

Davies et al. (1984) found I/O ratios of 0.7 ± 0.1 at an art gallery in rural Norwich, England, where the outside ozone concentrations ranged from 18

TABLE 5-13. SUMMARY OF REPORTED INDOOR-OUTDOOR OZONE RATIOS

Structure	Indoor-outdoor ratio (I/O)	Reference
Residence (with evaporative cooler)	0.60[a]	Thompson et al. (1973)
Office		Sabersky et al. (1973)
(air-conditioned; 100% outside air intake)	0.80 ± 0.10	
(air-conditioned; 70% outside air intake)	0.65 ± 0.10	
Residence	0.70	Sabersky et al. (1973)
Residence	0.50 to 0.70	Moschandreas et al. (1978)
Residence		Moschandreas et al. (1981)
(gas stoves)	0.19	
(all electric)	0.20	
Office	0.29	Moschandreas et al. (1978)
School room	0.19 (maximum concn.)	Berk et al. (1980)
Residence	0.10 to 0.25	Berk et al. (1981)
Residences (1 each)		Stock et al. (1983)
(air-conditioned)	0.00 to 0.09	
(100% outside air; no air conditioning)	1.0	
Residences (12) (air-conditioned)	0.21 (mean concn.) 0.12 (median concn.) 0.59 (maximum concn.)	Contant et al. (1985)
Art gallery (three modes of ventilation in each 24-hr period: recirculation, mixture of recirculated and outside air, and 100% outside air)	0.70 ± 0.10 (mean concn.)	Davies et al. (1984)

[a] Measured as total oxidants.

to 58 ppb in the 3-week study period. The interior of the modernistic gallery had few reactive surfaces (two plate glass walls and two walls and ceiling of painted aluminum, with minimal other walls and furnishings). In addition, ventilation cycled between recirculation air, a mixture of outside and recirculation air, and 100 percent outside air over each 24-hour period.

The results of all the studies cited above are shown in Table 5-13. These results are highly variable, to say the least. The variability is not surprising, however, considering the diversity of structures and locations included in the studies. In Table 5-13, the highest I/O, 1.0, was reported for a residence ventilated by outside air (Stock et al., 1983). The second-highest I/O, 0.80, was determined by smog-season measurements made in a multistory, air-conditioned building on the Pasadena campus of the California Institute of Technology (Sabersky et al., 1973). Air exchange in this building was at a rate of 10 changes per hour with 100 percent outside air (i.e., no recirculation of inside air). For another Cal Tech building, in which there was a mixture of 70 percent outside air and 30 percent recirculated inside air, Sabersky et al. (1973) found an indoor-outdoor ozone ratio of 0.65. The lowest indoor-outdoor ozone concentration ratios shown in Table 5-13 are those reported by Stock et al. (1983) for one residence; the indoor concentration recorded is barely above the limit of detection of the analyzer.

A relatively large number of factors can affect the difference in ozone concentrations between the inside of a structure and the outside air. In general, outside air infiltration or exchange rates, interior air circulation rates, and interior surface composition (e.g., rugs, draperies, furniture, walls) affect the balance between replenishment and decomposition of ozone within buildings (Thompson et al., 1973; Sabersky et al., 1973; Berk et al., 1980; Moschandreas et al., 1978). The rate at which exterior air enters a building depends on local wind speed and direction, on how well-sealed the building is, on how frequently doors and windows are opened, and on the operating characteristics and cycles of heating/air conditioning/ventilating systems. A significant factor that increases infiltration is an increasing temperature differential between warm interior air and cold outside air (Moschandreas et al., 1978), although a high differential would be unusual for a photochemical smog period. Moschandreas et al. (1978) reported exterior-interior exchange rates ranging from ten changes per hour in an office building to one change every 5 hours in a residence. At the higher exchange rates, inducted ozone remains at a level indoors that is closer to the outdoor level. As the exchange rate decreases, surface decomposition processes can result in progressively lower equilibrium ozone concentrations. Other factors, such as relative humidity, also affect decomposition. The half-life of ozone inside residences has been estimated at 2 to 6 minutes (Moschandreas et al., 1978; Mueller et al., 1973; Sabersky et al., 1973), while its half-life in an office environment has been estimated at 11 minutes (Mueller et al., 1973). These results are indicative of the relatively rapid reaction rate that can be expected for ozone in a building or room environment. The problem of I/O values in buildings was the subject of a model development program by Shair and Heitner (1974) in which they tried to account for ventilation and for losses by reactions and surface scavenging. Considering the research results shown in Table 5-13 and summarized by Yocom (1982), any estimates of indoor ozone exposures must be considered as having a large degree of probable variability.

Automobiles and other vehicles constitute another indoor environment in which people may spend appreciable amounts of time. As with buildings, the mode of ventilation and cooling helps determine the inside concentrations. Peterson and Sabersky (1975) reported ozone measurements made inside and outside a car traveling a freeway in southern California. Concentrations inside were higher when the air-conditioning was operating on "maximum" than when it was operating on "normal," largely because at higher air turnover rates ozone intake exceeded ozone decay. When windows were opened, an equilibrium between inside and outside ozone concentrations was established in about 3 minutes, with inside concentrations then remaining significantly lower than outside concentrations as the result of the exponential decay of ozone from contact with interior surfaces. Inside ozone concentrations were one-third or less of the outside concentrations ($I/O \leq 0.33$), on the average, under all ventilation and cooling conditions. Ozone concentrations measured outside the car were lower than those measured at nearby fixed sites, a result attributed to scavenging of ozone by nitric oxide. In the exposure study of Contant et al. (1985) in Houston, I/O ratios from 49 measurements inside vehicles were 0.44 for mean, 0.33 for median, and 0.56 for maximum concentrations measured. Driving routes and ventilation and cooling modes were not described.

Concentrations of ozone inside vehicles obviously depend first on the concentration outside and then on the various effects of cooling and ventilation conditions and surface decay. Thus, the titration of O_3 by NO on and near roadways is an important factor. The titration reaction is rapid but depends on the amount of NO emitted, which in turn depends on the amount of traffic on a given road or freeway. Rhodes and Holland (1981) found average ozone levels on the nine-lane freeway between Los Angeles and San Diego, which carries 200,000 cars each day, to be one-ninth to one-sixth the levels found 30 meters upwind.

At present there are no long-term monitoring data on indoor air pollutant concentrations that are comparable to the concentration data available for outdoor locations. Thus, for estimates of the exposure of building or vehicle occupants to ozone and other photochemical oxidants, it is necessary to rely on extrapolations of very limited I/O data such as those presented above and in Table 5-13.

5.5.2.4 Altitudinal and Latitudinal Variations. Concentrations of ozone vary with altitude and with latitude. These variations occur for a number of reasons, including the nature of the interchange mechanisms involved in stratospheric-tropospheric exchange, the decay of stratospheric ozone as it traverses the troposphere, and the known production of ozone in the apparently unpolluted free troposphere at certain altitude ranges above mean sea level (MSL). In addition, other meteorological, physical, and chemical factors contribute to the concentration gradients found with changes in altitude and latitude at the surface of the earth.

Among specific factors known to contribute to variations in ozone concentrations with altitude and latitude, and, to a much lesser extent, longitude, are the following:

1. Incursions of stratospheric ozone;
2. Global circulation patterns, along with accompanying altitudinal and geographic differences in atmospheric pressure, direction of prevailing winds, wind speeds, temperature, humidity, and precipitation;
3. Intensity and spectral distribution of sunlight; and
4. Meteorological factors, such as mixing heights, frequency and persistence of inversions, upslope flows in mountainous areas, and cloud cover and precipitation patterns.

Most of these factors were discussed in Chapter 3, as well as in the 1978 criteria document (U.S. Environmental Protection Agency, 1978). A few are briefly noted here to present an overview of the macroscale differences in ozone concentrations that may be expected. Concentration gradients found with increases in altitude at the earth's surface are presented in more detail because of their relevance for specific kinds of exposure assessments.

Latitudinal differences in ozone concentrations have been demonstrated. These are in part attributable to the variations, temporal as well as geographic, in actinic irradiance at the earth's surface. Both the intensity and the spectral distribution of sunlight have direct effects on the photochemical reactions that initiate and sustain oxidant formation (Chapter 3 and U.S. Environmental Protection Agency, 1978). The effect of latitude on ozone formation is significant during the winter but not during the summer, since in summer, for the contiguous United States, the maximum light intensity is fairly constant and the duration of the solar day varies only slightly with latitude. Light intensity varies somewhat with longitude in the summer, with the highest intensities occurring in the western states.

Incursions of stratospheric ozone also contribute to variations in ozone concentrations with latitude. These are expected to be strongest in the mid-latitudes of the northern hemisphere because of the nature of the mechanisms by which stratospheric-tropospheric exchange occurs.

The 1978 criteria document presented discussions of the effects of tropopause-folding events (TF) and of the seasonal tropopause adjustment (STA) and small-scale eddy transport (SSET) mechanisms on stratospheric-trospheric exchange. As described previously in Chapter 3 and in the 1978 document, TF events would be expected to produce sporadic increases in ground-level ozone concentrations, resulting from strong incursions of stratospheric ozone, in the southern and eastern United States (latitudes of $\lesssim$ 37°N and longitudes of $\lesssim$ 90°) (U.S. Environmental Protection Agency, 1978). The STA-produced incursions also occur in these latitudes. Both STA and TF produce incursions in the winter or early spring.

Logan et al. (1981) summarized earlier measurements of ozone in the lower troposphere. Hemispheric asymmetry is apparent in the data they presented, with higher concentrations occurring in the northern hemisphere than in the southern. Also apparent is a seasonal increase in lower-tropospheric ozone in the summer at mid-latitudes in the northern hemisphere. The authors noted, however, that ozone data for the lower troposphere are sparse, especially for the southern hemisphere. Compared with ozone data from two east-coast sites at mid-latitudes in the northern hemisphere, ozone data from one site in Australia showed (1) little seasonal variation at $\leq$3 km (MSL), (2) about 40 percent lower concentrations at 2 km (MSL) in summer, and (3) similar concentrations in autumn and winter. Altitudinal profiles of ozone concentrations for the tropical northern hemisphere (Panama, 9°N, and Hawaii, 19.5°N) show a considerably lower gradient with altitude than that seen at mid-latitudes (Oltmans, 1981; cited in Logan et al., 1981). Logan et al. (1981) noted the difficulty, given the sparseness of the data, of separating hemispheric effects from variations in concentrations attributable to other factors (e.g., oceanic, coastal, inland meteorology).

In a more recent report, the same investigators presented other data showing hemispheric differences in ozone concentrations and the seasonal distributions of those concentrations (McElroy et al., 1985). Ozone concentrations in the lower troposphere measured at Cape Grim, Tasmania (ca. 41°S), showed strong similarities, including seasonal distributions, to those measured at three different sites, at different longitudes, in Canada (latitudes of ca. 53°N to 59°N). Ozone concentrations from sites in West Germany, Switzerland, and the United States showed even greater similarity, both in level and seasonal distribution.

Although of interest and concern when estimating global ozone budgets, variations in ozone concentrations with latitude have little practical significance for assessing exposure within the contiguous United States. The effects on ozone concentrations of latitude, as well as longitude, within the contiguous states are minor.

A number of additional reports are available on the increase of tropospheric ozone concentrations with altitude (e.g., Kroening and Ney, 1962; Galbally and Roy, 1980). The data cited above showing latitudinal effects also show altitudinal effects, particularly at mid-latitudes in both the northern and southern hemispheres (Oltmans, 1981; cited in Logan et al., 1981). At mid-latitudes, the increase in background ozone concentrations rises rather sharply (from a spring-summer mixing ratio of about 40 to 60 ppb to one of about 100 ppb) between altitudes of about 8 and 12 km (ca. 5 to 7.4 mi, or ca. 26,400 to 39,600 ft). Between the surface and about 2 km (ca. 1.2 mi, or ca. 6600 ft), another relatively sharp increase in ozone concentrations is observed for the mid-latitudes (from a spring-summer mixing ratio of about 35 ppb to one of about 50 to 55 ppb) (Oltmans, 1981; cited in Logan et al., 1981). Other data corroborate these findings. Seiler and Fishman (1981) reported ozone measurements taken on flights in remote tropospheric air during July and August 1974. Their data also show that ozone concentrations increase with increasing altitude and in general substantiate the accepted view that the lower atmosphere and the surface of the earth act as ozone sinks.

Increases in ozone concentrations at higher altitudes are of potential concern relative to exposures sustained in-flight by airline passengers and employees on high-altitude flights (see Chapter 11). Air-filtration systems are employed on airplanes, however, that reduce ozone concentrations. Increases in concentrations with altitude at lower altitudes (e.g., in the zero to 2 km range) have potentially greater importance, since these gradients may affect forest ecosystems in mountainous areas. (It must be borne in mind, however, that atmospheric pressure decreases with altitude and thus, for a given concentration, the mass of ozone per cubic meter of air also decreases with altitude.) Contributors to increased ozone concentrations at the higher altitudes of relevance for forest ecosystems include stratospheric ozone intrusions and ozone transported aloft and conserved overnight in nocturnal inversions layers. The latter, in particular, may be an important consideration for the accurate assessment of the ozone exposures sustained by mountain forest ecosystems, as discussed below (see Chapter 7 also).

While a number of reports contain data on ozone concentrations at high altitudes (e.g., Coffey et al., 1977; Reiter, 1977b; Singh et al., 1977; Evans, 1985; Lefohn and Jones, 1986), fewer reports are available that present data for different elevations at the same locality. Studies by Berry (1964) and Miller and Ahrens (1969) are among earlier reports documenting ozone gradients with altitude in forested areas. Two more recent studies are discussed here because the investigators acquired and presented data on the diurnal patterns of ozone at those sites, as well as on differences in ozone concentrations at the respective altitudes. In addition, the two studies were conducted in different parts of the country and presented data that demonstrate differences in the meteorological influences on the concentrations found in the respective studies.

The mixed-conifer forest ecosystem of the San Bernardino Mountains in California is the most thoroughly studied forest ecosystem in the United States (see Chapter 7). In conjunction with vegetation and forest ecosystem studies conducted there in the 1960s and 1970s, a number of monitoring stations were established at different elevations on the south-facing slopes of the San Bernardino Mountains. The mountain range begins about 80 miles east of Los Angeles and its center is almost due east of Pasadena. The first four monitoring stations were established at Highland, City Creek, Mud Flat, and Rim Forest, located as shown in Figure 5-22.

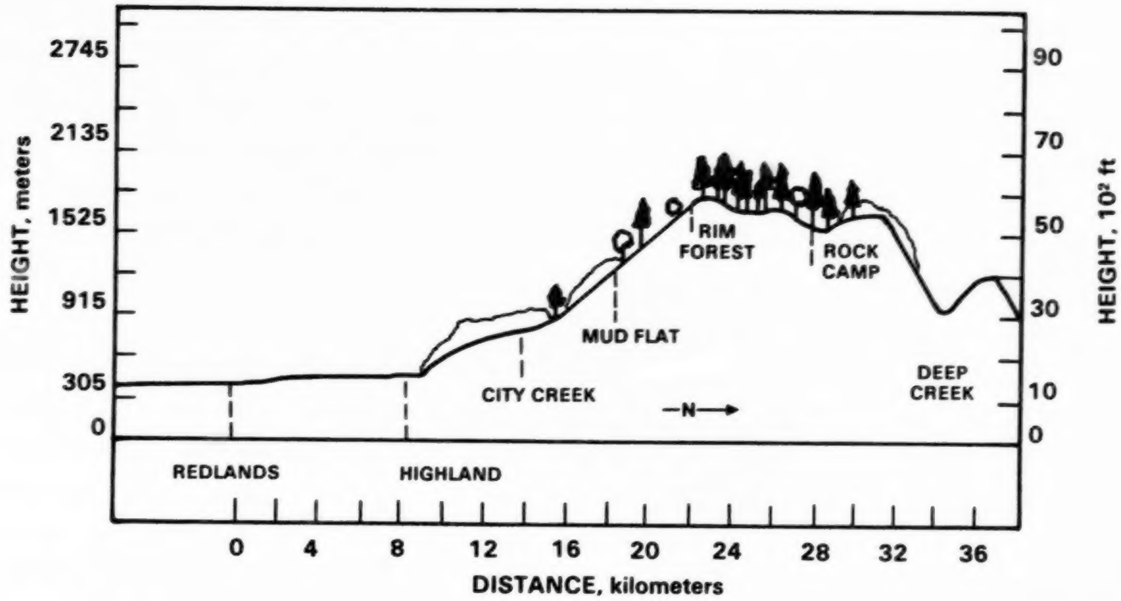

Figure 5-22. Altitudinal sequence of monitoring sites in the San Bernardino Mountains.

Source: Adapted from Miller et al. (1972).

Total oxidant, temperature, and relative humidity (RH) were measured continuously during 16 days in July and August at all but the Highland station (Miller et al., 1972). The vapor pressure gradient was calculated from RH and temperature data. The time of the daily peak oxidant concentration was progressively later at stations of higher elevation, as shown in Figure 5-23. Temperatures and vapor-pressure gradients were also progressively lower at higher elevations at the time of the oxidant peak. The average duration of oxidant concentrations exceeding 200 $\mu g/m^3$ (0.10 ppm) was 9, 13, 9, and 8 hr/day going from lower to higher stations for June, July, and August 1969. The longer duration at City Creek (elevation 817 m; 2680 ft) probably coincided with the zone where the inversion layer most often contacted the mountain slope. The oxidant concentrations rarely decreased below 98 $\mu g/m^3$ (0.05 ppm) at night on the slope of the mountain crest, whereas they usually decayed to near zero at the basin station (Highland, elevation 442 m; 1459 ft).

The vertical and horizontal distributions of oxidant air pollution in the Los Angeles Basin have been described by several investigators and presented in the 1978 criteria document (Blumenthal et al., 1974; Edinger, 1973; Edinger et al., 1972; Miller et al., 1972; as cited in U.S. Environmental Protection Agency, 1978). In Los Angeles, a marine temperature inversion layer frequently forms above the heavily urbanized metropolitan area and often extends inland as far as 144 km (90 miles), depending on season and time of day. Surface heating of air under the inversion increases with distance eastward in the basin and often disrupts the inversion by midmorning at its eastern edge. The marine temperature inversion layer encounters the mountain slopes, usually below 1200 m (4000 ft). In the morning, the temperature inversion often remains intact at this juncture, and air pollutants are confined beneath it. The heated mountain slopes act to vent oxidant air pollutants over the crest of the mountains and cause the injection of pollutants into the stable inversion layer horizontally away from the slope. Oxidant concentrations within the inversion are not uniform, but occur in multiple layers and strong vertical gradients. In some cases, the inversion may serve as a reservoir for ozone, which may arrive at downwind locations along the mountain slopes relatively undiluted because of a lack of vertical mixing within the inversion layer and a lack of contact with ozone-destroying material generated at the ground. The important result of the trapping of oxidant in these layers is its prolonged contact with high terrain at night.

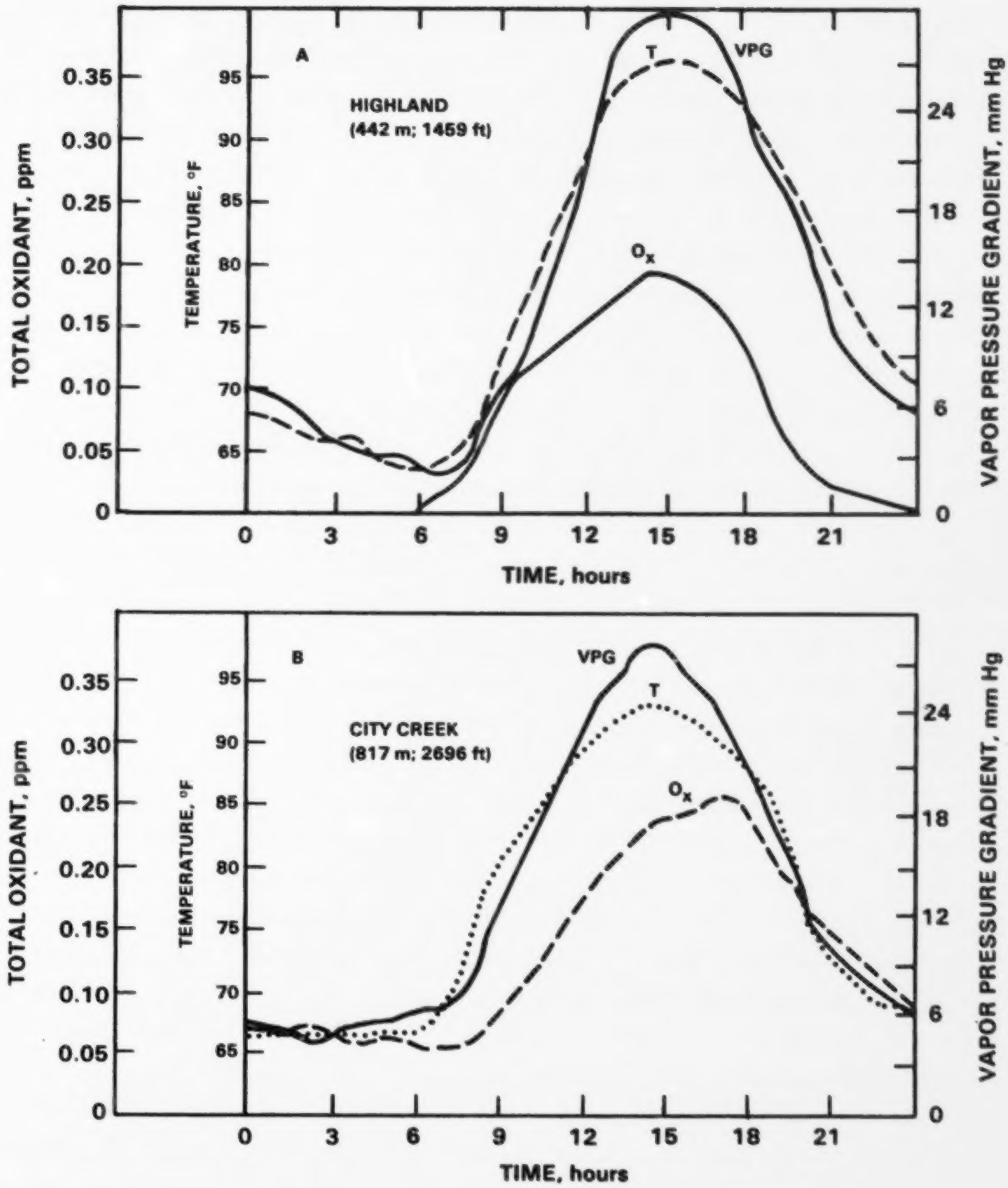

Figure 5-23. Relationship between elevation and diurnal patterns of total oxidant concentrations, temperature, and vapor pressure at four sites (A-D) in the San Bernardino Mountains, CA, July-August 1969.

Source: Miller et al. (1972).

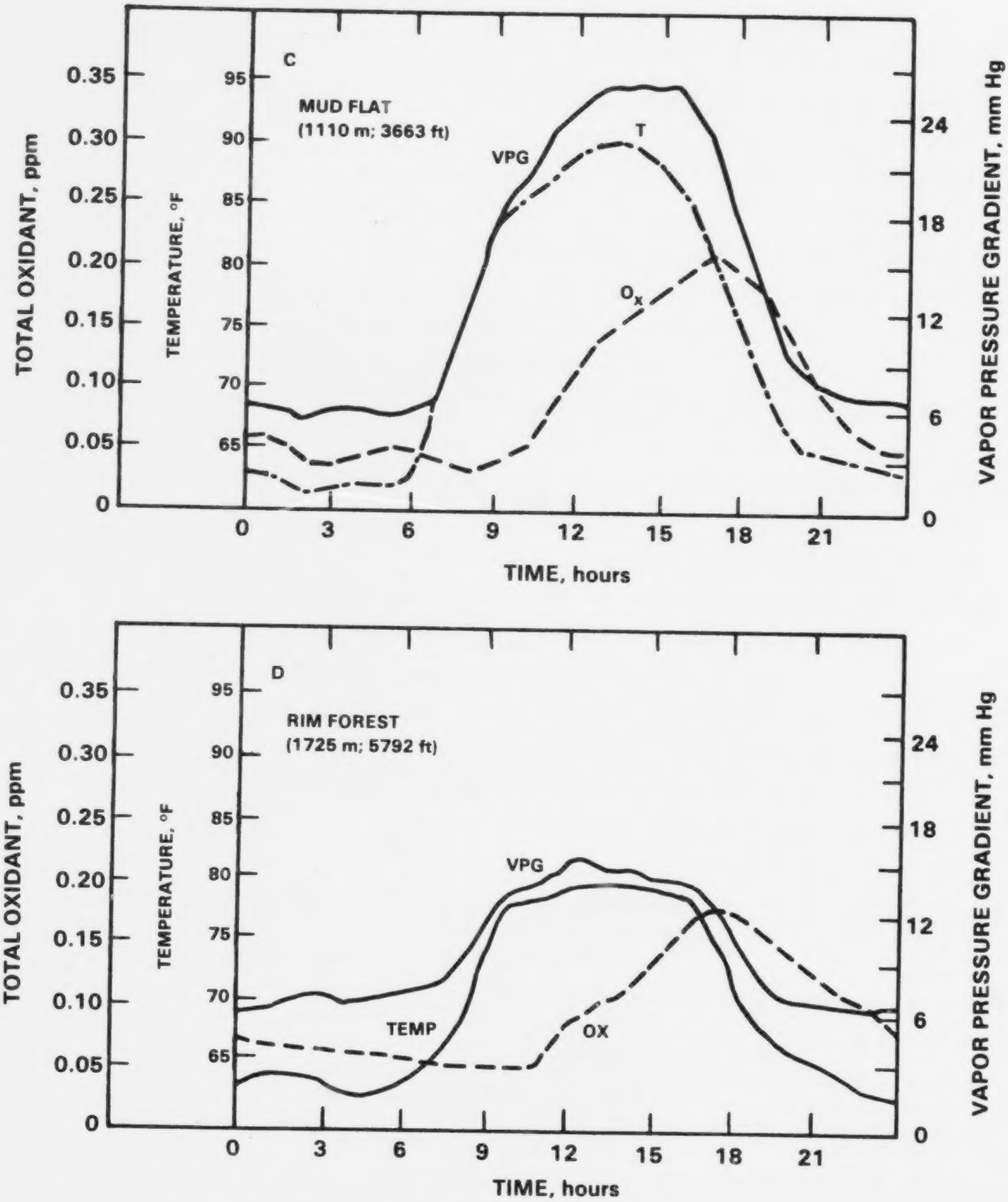

Figure 5-23 (Cont'd). Relationship between elevation and diurnal patterns of total oxidant concentrations, temperature, and vapor pressure at four sites (A-D) in the San Bernardino Mountains, CA, July-August 1969.

Source: Miller et al. (1972).

The studies in the Los Angeles Basin and the nearby San Bernardino Mountains underscore the importance of understanding the interactions between topography and local meteorology for specific areas. Consideration of those factors is essential for accurate exposure assessments at higher altitudes, especially in the absence of monitoring sites and adequate aerometric data.

Wolff et al. (1986) conducted a study of the effects of altitude on ozone concentrations at three sites located at three separate elevations on High Point Mountain in northwestern New Jersey. Ozone concentrations and temperature were measured at ground level at the respective sites. In addition, temperature and relative humidity were measured above the surface by balloon-borne sensors, with wind direction and speed data obtained by means of a tracking theodolite.

Data for several days (July 1975) indicate that in mid-day, when atmospheric mixing was good, vertical profiles were nearly constant, with concentrations increasing only slightly with elevation. Likewise, the daily ozone maxima were similar at different elevations. At night, however, ozone concentrations were nearly zero in the valley (the lowest-elevation site) and increased with elevation. Comparison of the ozone dosages at the three sites (number of hours > 0.08 ppm) showed that greater cumulative doses were sustained at the higher elevations (Table 5-14). Comparable data from an urban area (Bayonne, NJ) about 80 km southeast of High Point Mountain showed that the cumulative doses were higher at all three of the mountain sites than in the urban area (Table 5-14) (Wolff et al., 1986).

TABLE 5-14. COMPARISON OF OZONE CONCENTRATIONS AT THREE DIFFERENT ELEVATIONS, HIGH POINT MOUNTAIN, NJ, AND AT BAYONNE, NJ, JULY 1975

Location/elevation	1-hr max, ppb	24-hr mean, ppb	1-hr max, ppb	24-hr mean, ppb	No. hr ≥80 ppb
High Point, 500 m	66	49	130	81	13
High Point, 300 m	61	38	110	61	9
High Point, 140 m	59	26	120	52	9
Bayonne, sea level	69	33	119	48	7

Source: Wolff et al. (1986).

The maximum depth of the nocturnal inversion at High Point Mountain was about 900 m (ca. 2970 ft). Extrapolating from the gradient observed from the ground sites, Wolff et al. (1986) estimated that mountain peaks exceeding 900 m (2970 ft) would sustain exposures to relatively constant diurnal concentrations that would approximate the maximum ozone concentration found at the valley site. The investigators concluded from their concentration and meteorological data that elevated, mountainous sites in the eastern United States may be expected to be exposed to higher ozone dosages than valley sites throughout the year.

5.5.2.5 Vertical Gradients at Ground Level. Just as macroscale variations in ozone concentrations have been observed by measuring vertical and horizontal profiles at various altitudes, so too have microscale vertical variations at ground level been observed as a function of placement of sampling probes. Data drawn from a recent study on rural ozone concentrations illustrate the effects on concentration data of the placement of monitoring probes. These effects are pertinent for vegetation exposures, in particular, although the vertical gradient at ground level has obvious implications for human exposures as well.

Pratt et al. (1983) studied concentrations of ozone and oxides of nitrogen in the upper-midwestern part of the United States. Concentration data were obtained over 4 years by means of monitors placed at two different sampling heights (ca. 3 and 6, or 3 and 9 meters) at three air quality monitoring sites: LaMoure County, North Dakota; Traverse County, Minnesota; and Wright County, Minnesota. All stations were rural sites. The mean ozone concentrations did not differ greatly among the sites, but in at least some instances the mean differences between sampling heights were as large or larger than the differences among the scattered sites. Table 5-15 presents the mean ozone concentrations measured at two separate sampling heights (Pratt et al., 1983). Annual average concentrations were 1 to 3 ppb lower at the 3.05-meter height than at the 6.10 or 9.14-meter heights, reflecting the depletion of ozone near the surface. As might be expected, the gradient was especially conspicuous at night because of continued surface scavenging and a decrease in the rate of transfer from layers aloft. The concentrations of ozone occurring at these sites were near background in all years measured. In areas with higher ozone concentrations, one would expect to see larger absolute gradients between

TABLE 5-15. MEANS AND STANDARD ERRORS OF OZONE CONCENTRATIONS MEASURED OVER 4 YEARS AT TWO SAMPLING HEIGHTS AT THREE STATIONS IN THE RURAL, UPPER-MIDWESTERN UNITED STATES (ppb/v/v)

Site	Sampling height, m	Years					
		1977	1978	1979	1980	1981	1977-1981
LaMoure County, ND	3.05	22.97 ± 0.20 (6,413)[a]	35.30 ± 0.20 (15,218)	30.80 ± 0.16 (21,064)	34.98 ± 0.25 (17,157)	31.92 ± 0.26 (6,699)	32.26 (66,551)
	9.14	24.14 ± 0.19 (6,410)	35.67 ± 0.19 (15,220)	32.25 ± 0.15 (20,470)	37.53 ± 0.25 (17,157)	34.23 ± 0.26 (6,364)	33.82 65,597
Traverse County, MN	3.05	24.44 ± 0.19 (9,672)	35.2 ± 0.19 (22,675)	30.64 ± 0.17 (19,900)	34.66 ± 0.23 (22,629)	28.78 ± 0.23 (7,141)	32.09 (82,017)
	9.14	26.29 ± 0.19 (9,810)	36.77 ± 0.19 (22,624)	32.39 ± 0.16 (19,289)	37.60 ± 0.23 (22,625)	31.08 ± 0.22 (7,142)	34.21 (81,550)
Wright County, MN	3.05	-	34.64 ± 0.23 (17,437)	28.71 ± 0.18 (17,771)	34.27 ± 0.26 (18,222)	31.60 ± 0.24 (7,764)	32.42 (61,254)
	6.10	-	35.61 ± 0.23 (17,440)	29.27 ± 0.18 (17,775)	35.16 ± 0.27 (18,280)	32.28 ± 0.24 (7,766)	33.21 (61,261)

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[a] The numbers in parentheses refer to the number of hours of monitoring included in the reported values. Values are based on all valid data per site. For each sampling height at each site, values for three monitors separated by 76 m are included in the calculations. Monitoring was conducted only during the second half of 1977 and only until 30 June in 1981.

Source: Pratt et al. (1983).

monitors at different heights. In fact, the careful measurement of concentration gradients over distances of 1 to 10 meters above a surface is a recognized method for estimating the scavenging potential of the surface.

In this context, it should be noted that the dry deposition of ozone on various surfaces has been fairly extensively studied. Summaries on surface scavenging and other natural removal processes appeared in the previous criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978) and in the review by the National Research Council (National Research Council, 1977). Newer review articles on dry deposition and surface scavenging have been published by Wesely (1983) and Galbally and Roy (1980), among others.

5.6 CONCENTRATIONS OF PEROXYACETYL NITRATE AND PEROXYPROPIONYL NITRATE IN AMBIENT AIR

5.6.1 Introduction

As noted in the introduction to this chapter (Section 5.1), published data on the concentrations in ambient air of photochemical oxidants other than ozone are not comprehensive or abundant. Much more is known now, however, about their atmospheric concentrations than was known when the 1978 criteria document for ozone and other photochemical oxidants was published. Review of the data that follow will show that peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) are the most abundant of the non-ozone oxidants in ambient air in the United States other than the inorganic nitrogenous oxidants such as nitrogen dioxide (NO_2), and possibly nitric acid (HNO_3), in some areas. The inorganic nitrogenous oxidants found in ambient air are reviewed in air quality criteria documents on the nitrogen oxides and are not treated in this document except for the review of the role of nitric oxide (NO) and NO_2 in atmospheric photochemistry.

Available data show that PAN is toxic to vegetation and is potentially toxic to humans. No data indicating potentially adverse effects of PPN are available. It exists in trace quantities and apparently no research has ever been undertaken to determine its potential toxicity. At least one study (Heuss and Glasson, 1968) has reported that a higher homologue of the series, peroxybenzoyl nitrate (PBzN), like PAN, is a lachrymator. No unambiguous identification of PBzN in the ambient air of the United States has been made, however.

Given the information available on PAN, the concentrations of PAN that are of most concern are those to which vegetation could potentially be exposed, especially during daylight hours in agricultural areas; followed in importance by those both indoors and outdoors, in both urban and nonurban areas, to which human populations could potentially be exposed. Most of the available data on concentrations of PAN and PPN in ambient air are from urban areas. The levels to be found in nonurban areas will be highly dependent upon the transport of PAN and PPN or their precursors from urban areas, since the concentrations of the NO_x precursors to these compounds are considerably lower in nonurban than in urban areas.

The following sections present historical and recent data on the concentrations of PAN and, where available, on PPN, as well as the patterns those concentrations assume.

5.6.2 Historical Data

In the 1970 criteria document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970), concentrations for total oxidants and PAN were reported for Los Angeles and Riverside, California. In Los Angeles, composite diurnal data for PAN (obtained by GC-ECD) showed average peak 1-hr concentrations of about 40 ppb in September 1965 and about 60 ppb in October 1965. The September peaks occurred around noon and the October peaks occurred shortly after 1:00 p.m., with the difference in time possibly being a function of the temperature-dependence of PAN formation and persistence. In Riverside, two peak concentrations were observed in composite diurnal data, one of $\gtrsim$ 4 ppb around 10:00 a.m. and one of ~10 ppb between 4:00 and 6:00 p.m. Seasonal data from Riverside for June 1966 to June 1967 showed that PAN concentrations were highest in September 1966 and in March and June 1967.

Total oxidants (by Mast meter) in these Los Angeles sites reached a peak concentration (the same composite diurnal data as above) of close to 140 ppb in September 1965 at about the same hour of day as the PAN peak. In October, total oxidants peaked at nearly 200 ppb, again coinciding in time with peak PAN concentrations. In Riverside, the morning PAN peak preceded the oxidant peak (~110 ppb around noon) by almost 2 hours but the afternoon PAN peak trailed the afternoon oxidant peak (~160 ppb around 2:00 to 4:00 p.m.) by about 2 hours. The ozone/PAN ratio was variable from month to month but was generally lower from November through April than during the rest of the year, i.e., PAN was generally a greater percentage of the total oxidant during the November through April period.

In the 1978 criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978), additional PAN data for Los Angeles as well as two other cities were presented. Lonneman et al. (1976) measured PAN and total oxidants in Los Angeles in 1968. In 118 samples collected for the period 10:00 a.m. to 4:00 p.m. during the study, the median PAN concentration was 13 ppb and the average PAN concentration was 18 ppb. The median total oxidant concentration (measured by UBKI) was 97 ppb and the average was 117 ppb. Thus, the median oxidant/PAN ratio was 7.5 and the average oxidant/PAN ratio was 6.5; the median PAN concentration was 13.4 percent of the median total oxidant concentration, and the average PAN concentration was 15.4 percent of the average total oxidant concentration.

Lonneman et al. (1976) conducted similar studies in Hoboken, New Jersey, in 1970 and in St. Louis, Missouri, in 1973. Samples were measured during the period 10:00 a.m. to 4:00 p.m. over the course of the study. In Hoboken, PAN concentrations averaged 3.7 ppb. Ozone concentrations (measured by chemiluminescence) averaged 90.5 ppb. In St. Louis, PAN averaged 6.4 ppb, ozone (measured by chemiluminescence) averaged 50.1 ppb, and total oxidants (by UBKI) averaged 74.3 ppb.

From these 1966 through 1973 urban data, it is clear that PAN concentrations in urban areas are appreciably lower than those of ozone, even in the winter when PAN is higher relative to ozone than in summer.

In addition to urban data, the 1978 criteria document (U.S. Environmental Protection Agency, 1978) also included PAN concentration data from one nonurban agricultural area, Wilmington, Ohio (Lonneman et al., 1976). The maximum PAN concentration observed in 1500 samples taken during August 1974 was 4.1 ppb. The daily maximum PAN concentration rarely exceeded 3.0 ppb even though the daily maximum ozone concentration frequently exceeded 80 ppb.

Conclusions reached in the 1978 document were (1) that PAN concentrations are much lower in the ambient air of nonurban than of urban areas; and (2) that ozone/PAN or total oxidant/PAN ratios vary with location, such ratios being higher in nonurban areas than in urban; that is, PAN concentrations are a lower percentage of total oxidant concentrations in nonurban areas (U.S. Environmental Protection Agency, 1978). From data presented in the 1970 document, it may be concluded (1) that oxidant/PAN ratios vary with season;

(2) that PAN concentrations are lower than ozone concentrations in urban areas; and (3) that PAN and ozone concentrations exhibit similar but not identical diurnal patterns.

The historical data presented above have been given in some detail because the information about PAN conveyed by those data remains valid. Examination of the more recent data presented in subsequent sections shows that newer data extend and corroborate, for the most part, the findings of the older literature.

5.6.3 Ambient Air Concentrations of PAN and Its Homologues in Urban Areas

Additional studies on concentrations of PAN and its homologues in both urban and nonurban areas are now available. Newer data are presented in this section in summary form, where possible; and the individual studies or examples presented are merely a few of many, chosen to represent current knowledge regarding ambient air PAN concentrations and their patterns.

The existing literature on the concentrations in ambient air of the peroxyacyl nitrates, PAN and its higher homologues, has been compiled and examined in two recent review articles (Temple and Taylor, 1983; Altshuller, 1983). In the first, Temple and Taylor reviewed the concentrations of PAN in the ambient air in Europe, Japan, and North America in the context of the phytotoxicity of PAN. Altshuller, in the second, reviewed the published concentrations of PAN and of PPN in ambient air, also within and outside the United States. In addition, Altshuller analyzed the relationships to ozone of PAN and other photochemical reaction products. The reader is referred to these reviews for detailed information and for references therein.

Table 5-16 presents a summary of PAN concentrations observed in the ambient air of urban areas of the United States. Data in this table include the results of studies cited in Section 5.6.2 above, along with the results of newer studies. This table was derived from the reviews of Altshuller (1983) and Temple and Taylor (1983), as well as from a few additional sources (Jorgen et al., 1978; Lewis et al., 1983). The data are summarized in the table by region of the United States and by date, with the newer studies reported first for each region.

Because of variations in diurnal patterns of PAN by location and season, and because no national, uniform aerometric data base for PAN exists, few of the data reported in Table 5-16 are really comparable. Thus, data in this table lend themselves to general conclusions but not to the analysis of trends

TABLE 5-16. SUMMARY OF CONCENTRATIONS OF PEROXYACETYL NITRATE IN AMBIENT AIR IN URBAN AREAS OF THE UNITED STATES

Site	Time of yr	Yr	Hours sampled	No. days sampled	PAN concentrations, ppb Method^a	Avg.	Max.	Monthly mean	Original reference
West									
Riverside, CA	All year	1980	8 a.m.-8 p.m.	365	GC-ECD	NA^b	41.6	4.9	Temple and Taylor (1983)
W. Los Angeles, CA	June	1980	6:35 a.m.-1:35 p.m.	2	LP-FTIR	7	16	NA	Hanst et al. (1982)
Claremont, CA	Sept.-Oct.	1980	24 hr/day	11	GC-ECD	13	47	NA	Grosjean (1983)
Claremont, CA	Aug.-Sept.	1979	Morning to late evening	8	GC-ECD	4	11	NA	Tuazon et al. (1981a)
Claremont, CA	Oct.	1978	Late morning to late evening	5	LP-FTIR	6	37	NA	Tuazon et al. (1981a; 1981b)
Riverside, CA	Apr., May	1977	24 hr/day	10	GC-ECD	1.6	5.7	NA	Singh et al. (1979)
Riverside, CA	July, Aug., Oct.	1977	Late morning to evening	10	LP-FTIR	7	18	NA	Tuazon et al. (1980)
Riverside, CA	All year	1975 (May)- 1976 (Oct.)	24 hr/day	533	GC-ECD	3.6	32	NA	Pitts and Grosjean (1979)
Riverside, CA	Oct.	1976	Late morning to early evening	3	LP-FTIR	9	18	NA	Tuazon et al. (1978)
West Covina, CA	Aug., Sept.	1977	23 hr/day	24	GC-ECD	9	20	NA	Spicer (1977)
West Covina, CA	Aug., Sept.	1973	NA	NA	GC-ECD	NA	46	8.8	Spicer (1977)
Pasadena, CA	July	1973	7 a.m.-4:30 p.m.	3	LP-FTIR	30	53	NA	Hanst et al. (1975)
Riverside, CA	Aug.-Apr.	1967-1968	24 hr/day	273	GC-ECD	NA	58	4.6	Taylor (1969)
Downtown Los Angeles, CA	Sept.-Nov.	1968	10 a.m.-4 p.m.	NA	GC-ECD	8	68	NA	Lonneman et al. (1976)

TABLE 5-16 (continued). SUMMARY OF CONCENTRATIONS OF PEROXYACETYL NITRATE IN AMBIENT AIR IN URBAN AREAS OF THE UNITED STATES

Site	Time of yr	Yr	Hours sampled	No. days sampled	PAN concentrations, ppb				Original reference
					Method[a]	Avg.	Max.	Monthly mean	
Salt Lake City, UT	July-Sept.	1966	7 a.m.-3 p.m.	-	GC-ECD	-	54	4.4	Tingey and Hill (1968)
Los Angeles, CA	Sept.-Oct.	1965	8 a.m.-1 p.m.	35	GC-ECD	31	214	38 (Sept.) 40 (Oct.)	Mayrsohn and Brooks (1965)
Downtown Los Angeles, CA	July-Oct.	1960	9 a.m.-Noon	9	IR	~20	70	-	Renzetti and Bryan (1961)
Southwest									
Houston, TX	Oct.	1977	8 a.m.-8 p.m.	-	GC-ECD	-	15.6	-	Jorgen et al. (1978)
Houston, TX	July	1976	24 hr/day	22	GC-ECD	0.4	11.5	-	Westberg et al. (1978)
Midwest									
Dayton, OH (Huber Heights, OH)	July, Aug.	1974	24 hr/day	20	GC-ECD	0.7	10	-	Spicer et al. (1976)
St. Louis, MO	June-Aug.	1973	23 hr/day	26	GC-ECD	1.8	19	-	Spicer (1976)
St. Louis, MO	Aug.	1973	8 to 24 hr/day	12	GC-ECD	6.3	25	-	Lonneman et al. (1976)
East									
New Brunswick, NJ	All year	1978 (Sept.) -1980 (May)	24 hr/day (9600 1-hr values)	400	GC-ECD	0.5	10.6	-	Lewis et al. (1983)
New Brunswick, NJ[e]	Sept.-Dec.	1978	8 a.m.-6 p.m.		GC-ECD	-	10.5	2.7	Brennan (1980)
Hoboken, NJ	June, July	1970	10 a.m.-4 p.m.		GC-ECD	-	9.9	3.7	Lonneman et al. (1976)

[a] GC-ECD, gas chromatography with electron-capture detector; LP-FTIR, long-path Fourier-transform infrared spectroscopy; IR, infrared spectroscopy.

[b] Not available.

[c] Subset of data reported by Lewis et al. (1983), cited in table above.

Source: Altshuller (1983); Temple and Taylor (1983); Lewis et al. (1983); Jorgen et al. (1978).

over the past decade and a half or necessarily to analysis of between-city or between-region similarities or differences. For example, concentrations of PAN in Los Angeles appear to have been a great deal higher in 1965 (Mayrsohn and Brooks, 1965) than in 1980 (Hanst et al., 1982) for nearly the same time of day, but the 1965 concentrations were measured in September and October and the 1980 concentrations were measured in June. Other data from California indicate that September and October are more likely to be part of the smog season there than June. A comparison by Temple and Taylor (1983) of PAN concentrations in Riverside in 1980 with those in 1967 and 1968 indicates little difference. Again, however, the sampling periods were not identical relative to averaging time or time of year. Tabulated data from Temple and Taylor (1983) have been plotted in Figure 5-24.

In addition to compiling existing data on the concentrations of PAN in ambient air, Altshuller (1983) also related PAN concentrations to ozone concentrations where data for both exist. It must be borne in mind for this review, as well, that sampling periods (years, time of year, number of measurements) are not identical and in many cases are not even similar between studies (see Table 5-16). Neither are the averaging times over which samples were collected and calculated within respective studies identical or even necessarily similar. Nevertheless, the data of Altshuller constitute a comprehensive review and examination of the relationships among respective photochemical oxidants in urban areas of the United States. Concentrations of PAN as a percentage of ozone concentrations are given in Table 5-17, but Table 5-16 should be consulted for information on sampling periods and averaging times.

The existence of peroxybenzoyl nitrate (PbzN) in ambient air of urban areas was postulated in the 1978 criteria document for ozone and other oxidants (U.S. Environmental Protection Agency, 1978), but PBzN has not been clearly identified in ambient air in the United States. Hanst et al. (1982) estimated that as much as 2 ppb PBzN would be clearly detectable in FTIR measurements but reported no clear absorption band for PBzN in their measurements during a smoggy period in Los Angeles. They estimated an upper limit of 1 ppb PBzN during their 1980 study (the maximum ozone concentration was 272 ppb and the maximum PAN concentration was 16 ppb during that period).

The only homologue of PAN that has been unambiguously identified in ambient air in the United States is peroxypropionyl nitrate (PPN). In his

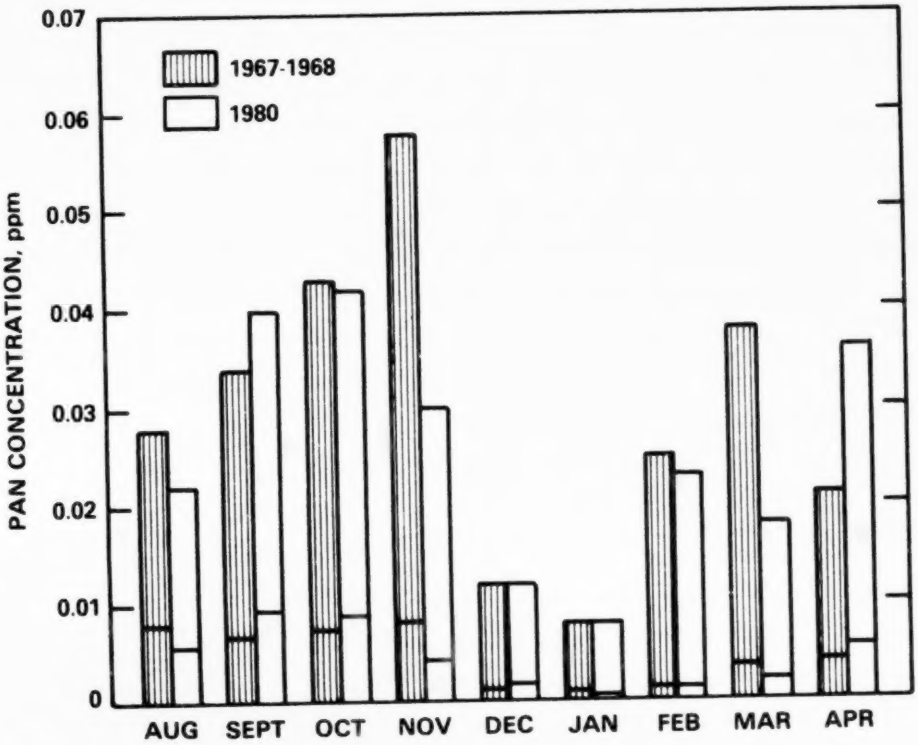

Figure 5-24. Comparison of monthly daylight average and maximum PAN concentrations at Riverside, CA, for 1967-1968 and 1980.

Source: Derived from Temple and Taylor (1983).

TABLE 5-17. RELATIONSHIP OF OZONE AND PEROXYACETYL NITRATE AT URBAN AND SUBURBAN SITES IN THE UNITED STATES

Site/year	PAN/O_3, % Avg.	PAN/O_3, % At O_3 peak	Reference
California			
Downtown Los Angeles, 1960	8	7	Renzetti and Bryan (1961)
Downtown Los Angeles, 1965	NA	7	Mayrsohn and Brooks (1965)
Downtown Los Angeles, 1968	13	NA[a]	Lonneman et al. (1976)
West Los Angeles, 1980	9	6	Hanst et al. (1982)
Pasadena, 1973	10	8	Hanst et al. (1975)
West Covina, 1977	20	12	Spicer (1977)
Claremont, 1978	7	6	Tuazon et al. (1981a, 1981b)
Claremont, 1979	4	4	Tuazon et al. (1981a)
Riverside, 1967-1968	8	NA	Taylor (1969)
Riverside, 1975-1976	9	5	Pitts and Grosjean (1979)
Riverside, 1976	5	4	Tuazon et al. (1978)
Riverside, 1977	4	4	Tuazon et al. (1980)
Riverside, 1977	4	NA	Singh et al. (1979)
Southwest			
Houston, TX, 1976	3	3	Westberg et al. (1978)
Midwest			
St. Louis, MO, 1973	13	NA	Lonneman et al. (1976)
St. Louis, MO, 1973	5	5	Spicer (1977)
Dayton, OH, 1974 (Huber Hts, OH)	2	1	Spicer et al. (1976)
East			
Hoboken, NJ, 1970	4	NA	Lonneman et al. (1976)
New Brunswick, NJ, 1978-1980	4	2	Brennan (1980)

[a] Not available.

Source: Adapted from Altshuller (1983).

review of existing literature, Altshuller (1983) compiled data on the concentrations of PPN in ambient air in urban areas. In addition, he calculated ratios of the concentrations of PPN and PAN. His data, expressed as percentages [(PPN/PAN) x 100], are presented as Table 5-18 (Altshuller, 1983).

As Altshuller has pointed out, average PPN concentrations are 10 to 30 percent of the average PAN concentrations shown in Table 5-18 except for those reported for San Jose (8 percent) and Oakland (42 percent). The maximum PPN concentrations reported are highly variable, however, ranging from 0.13 ppb in San Jose (August 1978) to 6.0 ppb in Riverside (month and year as well as sampling period of day unknown). Thus, the PPN/PAN ratio at maximum concentrations of PPN is highly variable, as well. Among more recent data, the maximum PPN concentration was 5.0 ppb in St. Louis in August 1973. Note, however, that the sampling period in St. Louis was 10:00 a.m. to 3:30 p.m. Depending upon temperature, concentrations of precursors, and other factors, a true PPN maximum may or may not have occurred by 3:30 p.m.

Table 5-19 presents PAN and PPN concentrations reported by Singh et al. (1981) for three cities, Los Angeles, Oakland, and Phoenix; as well as PPN concentrations as percentages of PAN concentrations (PPN/PAN x 100). Comparison of the data from these three cities helps demonstrate the variability of PPN and PAN concentrations with location.

5.6.4 Ambient Air Concentrations of PAN and Its Homologues in Nonurban Areas

Data on the concentrations of PAN and PPN in agricultural and other nonurban areas of the United States are sparse. They include data from the study done by Lonneman et al. (1976) in Wilmington, Ohio, in August 1974, and cited earlier in Section 5.6.2. In that study, measurements made by GC-ECD from 10:00 a.m. to 4:00 p.m., local time, showed a maximum concentration for the study period of 4.1 ppb. The average daily maximum was 2.0 ppb. While the 4:00 p.m. cutoff used by Lonneman et al. (1976) could possibly have resulted in missing some peak PAN concentrations, especially in transported air masses, the data are within the range reported by Westberg et al. (1978) and by Spicer and Sverdrup (1981) for 24-hour measurements at nonurban sites. At the Sheldon Wildlife Reserve, Texas, Westberg et al. (1978) found a 24-hour average PAN concentration of 0.64 ppb and a maximum concentration of 2.8 ppb for the study period (October). Spicer and Sverdrup (1981) found a 24-hour average PAN

TABLE 5-18. AMBIENT AIR MEASUREMENTS OF PEROXYPROPIONYL NITRATE (PPN) CONCENTRATIONS BY ELECTRON CAPTURE GAS CHROMATOGRAPHY AT URBAN SITES IN THE UNITED STATES

Site	Period of measurement/ no. of days (n)	Period of day	PPN, ppb		PPN/PAN, %		Reference
			Avg.	Max.	Avg.	Max.	
Los Angeles, CA	April 1979 (13)	24 hr	0.7	2.7	15	16	Singh et al. (1981)
Riverside, CA	NA[a] (1)	NA	NA	6	NA	12	Darley et al. (1963)
Riverside, CA	April-May	24 hr	0.3	1.8	21	32	Singh et al. (1979)
Riverside, CA	July 1980 (13)	24 hr	0.2	0.9	16	16	Singh et al. (1981)
San Jose, CA	August 1978 (7)	24 hr	0.08	0.13	8	10	Singh et al. (1979)
Oakland, CA	June-July 1979 (13)	24 hr	0.15	0.5	28	42	Singh et al. (1981)
Phoenix, AZ	April-May 1979 (14)	24 hr	0.09	0.33	12	9	Singh et al. (1982)
Denver, CO	June 1980 (14)	24 hr	0.05	0.32	10	3	Singh et al. (1982)
Houston, TX	May 1980 (12)	24 hr	0.11	0.63	14	25	Singh et al. (1982)
St. Louis, MO	10 Aug. 1973 (1)	1000-1530 (LT[b])	3.0	5.0	17	20	Lonneman et al. (1976)
St. Louis, MO	May-June, 1980 (9)	24 hr	0.66	0.25	23	28	Singh et al. (1982)
Chicago, IL	April-May, 1981 (13)	24 hr	0.05	0.13	12	8	Singh et al. (1982)
Pittsburgh, PA	April 1981 (11)	24 hr	0.05	0.07	17	10	Singh et al. (1982)
Staten Island, NY	March-April 1981 (11)	24 hr	0.20	3.1	27	80	Singh et al. (1982)

[a] Not available.

[b] Local time.

Source: Altshuller (1983).

TABLE 5-19. CONCENTRATIONS OF PEROXYACETYL AND PEROXYPROPIONYL NITRATES IN LOS ANGELES, OAKLAND, AND PHOENIX, 1979[a] (ppb)

	Los Angeles			Oakland			Phoenix		
Value	PAN	PPN	PPN/PAN, %	PAN	PPN	PPN/PAN, %	PAN	PPN	PPN/PAN, %
Mean	4.98	0.72	14	0.36	0.159	42	0.78	0.09	12
Std. dev.	4.48	0.67	-	0.42	0.12	-	0.77	0.08	-
Maximum	16.82	2.74	16	1.85	0.50	27	3.72	0.33	9
Minimum	0.03	ND[b]	-	0.05	ND[b]	-	ND[b]	ND[b]	-

[a] Measurements were made by gas-phase coulometry.

[b] Not detectable.

Source: Singh et al. (1981).

concentration of 0.50 ppb and a maximum of 6.5 ppb for the study period (July and August) at Van Hiseville, New Jersey, in the New Jersey pine barrens; and Spicer et al. (1983) reported averages of 0.46 ppb at a nonurban site in Indiana (Huntington Lake) and 0.74 at a nonurban site in east central Missouri (42 km west of St. Louis).

In contrast with these values, 24-hour average concentrations of PAN at one nonurban and four remote sites (see Table 5-20) were reported by Singh et al. (1979) to range from 0.08 to 0.30 ppb, with maxima at those sites ranging from 0.22 to 0.83 ppb. The Texas, Ohio, and New Jersey sites sustained higher PAN concentrations than the nonurban sites where Singh et al. (1979) measured PAN. The higher concentrations may reflect the influence at those sites of nearby metropolitan areas.

Concentrations of PAN have recently been reported by Singh and Salas (1983) for a Pacific marine site, Point Arena, California, at which earlier measurements were also made and reported by Singh et al. (1979) (see Table 5-19). Data collected in August 1982 showed concentrations of PAN ranging from 0.01 to 0.12 ppb during the 5-day study period. The average concentration for the period was 0.032 ± 0.024 ppb. Winds were west-to-northwest 90 percent of the time and northerly the rest of the time. Modeled trajectories confirmed that air masses passing over the site were of a marine origin. The site is thought to be free of manmade pollutants.

Data from two nonurban sites in Canada are of interest even though they are outside the United States. Cherniak and Corkum (1981; cited in Temple and Taylor, 1983) measured PAN at a nonurban site in Simcoe, Ontario, Canada, for 6 months. Measurements made by GC-ECD showed monthly means of <2 ppb and a maximum concentration during the study of 5.6 ppb. At a remote site in the Kananaskis Valley of Alberta, Canada, monthly mean concentrations were <1 ppb for samples taken at half-hour intervals, 24 hr/day, for 110 days (Peake et al., 1983). The site, located at the base of a mountain range and about 50 miles west of Calgary, is thought to be free of manmade pollutants, including transported pollutants.

5.6.5 Temporal Variations in Ambient Air Concentrations of Peroxyacetyl Nitrate

5.6.5.1 Diurnal Patterns. Concentration data obtained in the 1960s were briefly discussed in Section 5.6.2, where it was noted that the first criteria

TABLE 5-20. CONCENTRATIONS IN AMBIENT AIR OF PEROXYACETYL AND PEROXYPROPIONYL NITRATES AND OZONE AT NONURBAN REMOTE SITES IN THE UNITED STATES (ppb)

Site	Reference	Nature of site	Period of measurement and no. of days (n)	Period of day	Average concentrations			Maximum concentrations			Avg. PAN/ Avg. O_3, %
					PAN	PPN	O_3	PAN	PPN	O_3	
Mill Valley, CA	Singh et al. (1979)	Maritime	Jan. 1977 (12)	24 hr	0.30	0.04	38	0.83	0.11	0.55	0.8
Point Arena, CA	Singh et al. (1979)	Clean-maritime	Aug.-Sept. 1978 (7)	24 hr	0.08	ND[a]	ND[a]	0.28	ND[a]	ND[a]	ND[a]
Badger Pass, CA	Singh et al. (1979)	Remote-high altitude	May 1977 (10)	24 hr	0.13	0.05	46	0.22	0.09	54	0.3
Reese River, NV	Singh et al. (1979)	Remote-high altitude	May 1977 (7)	24 hr	0.11	0.04	39	0.26	0.09	56	0.3
Jetmore, KA	Singh et al. (1979)	Rural-continental	June 1978 (7)	24 hr	0.25	ND[a]	31	0.52	ND[a]	53	0.8
Sheldon Wildlife Reserve, TX	Westberg et al. (1978)	Rural-continental	October 1978 (9)	24 hr	0.64	ND[a]	47	2.8	ND[a]	148	1.4
Wilmington, OH	Lonneman et al. (1976)	Rural-continental	August 1974 (9)	10:00 a.m.-4:00 p.m.	NA[b]	ND[a]	NA[b]	4.1	ND[a]	107	NA[b]
Van Hiseville, NJ	Spicer and Sverdrup (1981)	Rural-continental	July-Aug. 1979 (31)	24 hr	0.50	ND[a]	36	6.5	ND[a]	161	1.4

[a] Not determined.

[b] Measured, but results not given in the reference.

Source: Altshuller (1983).

document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970) reported concentrations and patterns for PAN that remain valid now. In that document, the general proximity in time of PAN and oxidant peaks was shown in data from Los Angeles and Riverside, California. Maximum PAN concentrations, although varying from location to location, generally occurred in midday; i.e., late morning to mid-afternoon. Figures 5-25 and 5-26, taken from the 1970 criteria document (U.S. Department of Health, Education, and Welfare, 1970), graphically present the diurnal patterns of PAN in Los Angeles in 1965 and in Riverside in 1966. The occurrence of the second PAN peak in Riverside, which appears to trail a second total oxidant peak by an hour or two, was ascribed to transport, as verified by the occurrence of maximum oxidant concentrations at three receptor sites east of West Los Angeles (downtown Los Angeles, Azusa, and Riverside), at times that corresponded, wind speed factored in, with respective distances from West Los Angeles.

Examples drawn from recent data substantiate that the general diurnal pattern (as it appears in composite diurnal data averaged over a week, a month, or longer) remains the same as the pattern established by data obtained in the mid-1960s.

Using FTIR spectroscopy, Tuazon and coworkers (Tuazon et al., 1978, 1980, 1981b) measured concentrations of PAN at Claremont and Riverside, California, over a 5-year period. Concentrations of PAN ranged from about 5 to 40 ppb over the course of the study. The diurnal profiles for PAN and ozone at Claremont are shown for 2 days of a multiday smog episode in October 1978 in Figure 5-27 (Tuazon et al., 1981b). Note the qualitative relationship of the two pollutants, with the peak concentrations of the two occurring almost simultaneously. The relationship between PAN and ozone concentrations and behavior in the atmosphere is neither constant nor monotonic, however, as is borne out by the slight differences in time of occurrence of their peak concentrations but especially by the persistence of somewhat elevated PAN concentrations before return to "baseline" levels. It appears that PAN concentrations, in this instance at least, closely parallel the nitric acid (HNO_3) concentrations, persisting after ozone concentrations have subsided. The percentage of PAN relative to ozone differed slightly at the peak concentrations of the two on the 2 days. On October 12, the peak PAN concentration was close to 6 percent of the peak ozone concentration; on October 13, the peak PAN concentration was nearly 8 percent of the peak ozone concentration.

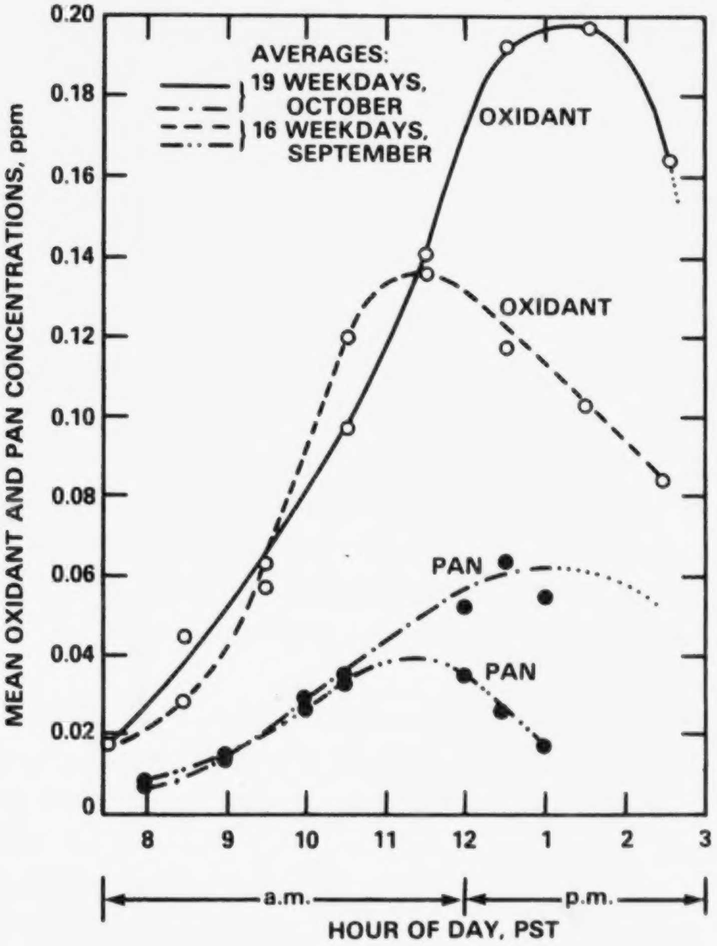

Figure 5-25. Variation of mean 1-hour oxidant and PAN concentrations, by hour of day, in downtown Los Angeles, 1965.

Source: U.S. Department of Health, Education, and Welfare (1970).

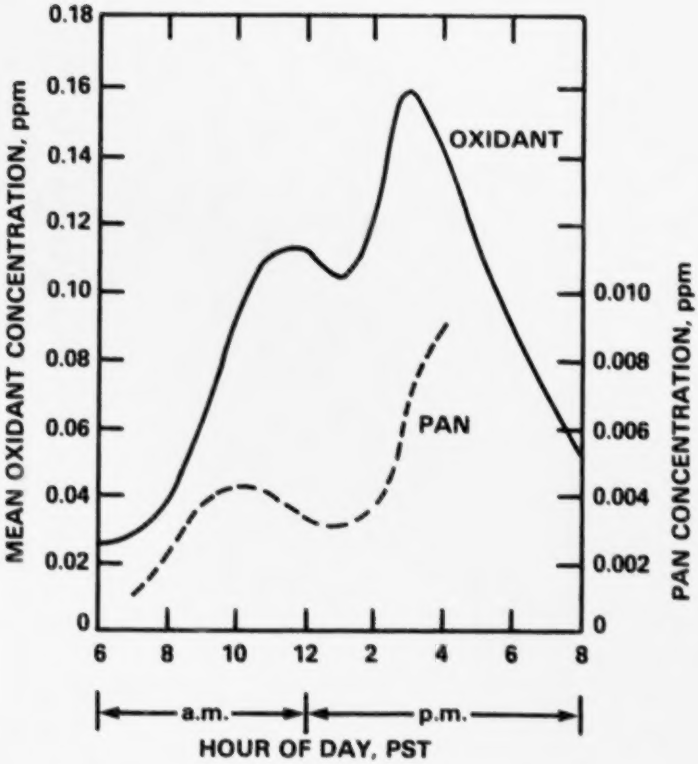

Figure 5-26. Variation of mean 1-hour oxidant and PAN concentrations, by hour of day, Air Pollution Research Center, Riverside, CA, September, 1966.

Source: U.S. Department of Health, Education and Welfare (1970).

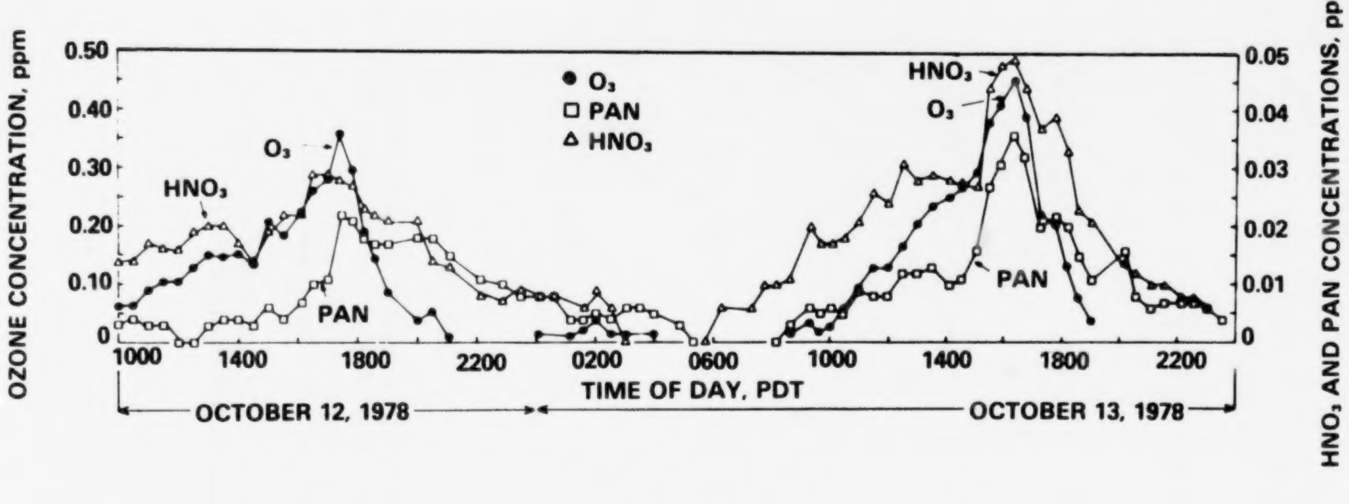

Figure 5-27. Diurnal profiles of ozone and PAN at Claremont, CA, October 12 and 13, 1978, 2 days of a multi-day smog episode.

Source: Tuazon et al. (1981b).

5.6.5.2 Seasonal Patterns. Seasonal differences in PAN concentrations were alluded to in Section 5.6.3 and mean and maximum PAN concentrations were presented by month for 2 years (1967-1968 and 1980) for Riverside, California, in Figure 5-24. That seasonal differences exist in PAN concentrations was also documented in the 1970 criteria document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970). Total oxidants and PAN were monitored for 13 months in Riverside, California. The oxidant concentrations were obtained by continuous Mast meter measurements, 24 hr/day. Concentrations of PAN were measured in sequential samples analyzed by GC-ECD from 6:00 a.m. to about 4:00 or 5:00 p.m. The data are not strictly comparable, since the shorter, daylight averaging time for PAN would be expected to result in somewhat higher mean concentrations of PAN than would be obtained across a 24-hour averaging period. Nevertheless, the patterns given in Figure 5-28 are of interest and demonstrate that peak PAN concentrations can constitute a higher percentage of the peak ozone concentrations during winter months than during the rest of the year. This observation is still valid (Spicer et al., 1983) and has been attributed by Lewis et al. (1983) and by Holdren et al. (1984) to greater PAN stability in the winter months because of cooler temperatures (Cox and Roffey, 1977). The possibility, however, that the somewhat greater NO_x emissions of the winter heating season also contribute to this phenomenon should not be overlooked.

Data from one additional study complement the older data already presented on diurnal and seasonal patterns (Section 5.4.2). Lewis et al. (1983) measured PAN and ozone concentrations from September 25, 1978, to May 10, 1980, in New Brunswick, New Jersey. Average (10-hr and 24-hr) and maximum concentrations of both pollutants are given in Table 5-21 by month of the year (Lewis et al., 1983). Note that the highest monthly mean concentrations, both the 10-hr and 24-hr means, occurred during the smog season (August and September) but that the next highest occurred in October and February, respectively. Average diurnal profiles were obtained during this same study and are shown, by month, in Figure 5-29 (Lewis et al., 1983).

5.6.6 Spatial Variations in Ambient Air Concentrations of Peroxyacetyl Nitrate

5.6.6.1 Urban-Rural Gradients and Transport of PAN. As noted earlier, precursors to PAN, especially NO_2, are lower in nonurban than in urban areas, such that little local formation is expected in nonurban areas. Available data on

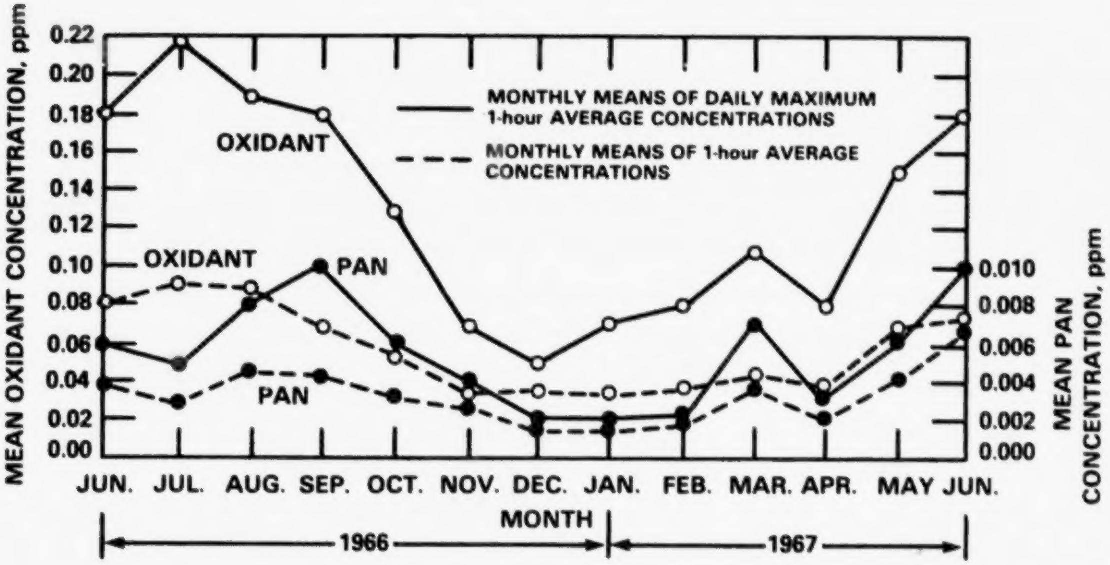

Figure 5-28. Monthly variation of oxidant (Mast meter, continuous 24-hr) concentrations and PAN (GC-ECD, sequential, 6:00 a.m. to 4:00-5:00 p.m.) concentrations, Air Pollution Research Center, Riverside, CA, June 1966 - June 1967.

Source: U.S. Department of Health, Education, and Welfare (1970).

TABLE 5-21. PAN AND OZONE CONCENTRATIONS IN AMBIENT AIR, NEW BRUNSWICK, N.J., FOR SEPTEMBER 25, 1978, TO MAY 10, 1980

Month	PAN concentration, ppb			O_3 concentration, ppb		
	24-hr average	10-hr average	Hourly maximum	24-hr average	10-hr average	Hourly maximum
January	0.12	0.19	1.3	11.5	15.5	34
February	0.61	0.69	4	17.2	23.2	40
March	0.36	0.41	1.3	23	29.1	58
April	0.45	0.57	2.5	28.5	37.3	80
May	0.23	0.28	1	31.4	40.9	78
June[a]	0.09	0.17	0.8	NA	NA	NA
July	0.26	0.44	3.5	37.5	57.6	130
August	1.17	1.63	10.6	37.4	55.9	145
September	1.04	1.41	7.5	22.4	33.9	110
October	0.93	1.08	5.8	15.8	22.6	68
November	0.25	0.31	3.5	11.6	15.8	40
December	0.57	0.62	2.5	9.7	12.8	35

[a] These results are lower than expected; however, there was no evidence of instrument malfunction.

Source: Lewis et al. (1983).

PAN concentrations indicate clearly that they are lower in nonurban areas than in urban (Section 5.5.3). It should be noted, however, that few data exist on concentrations in agricultural areas and that the possibility that PAN is transported is therefore important in assessing exposures of vegetation to PAN. Lonneman et al. (1976) and Nieboer and Van Ham (1976), in studies cited in the 1978 criteria document (U.S. Environmental Protection Agency, 1978), reported the transport of PAN. The more recent study by Nielsen et al. (1981) has confirmed that PAN can be present at relatively high concentrations in photochemically polluted air after long-range transport. Variations in concentrations of PAN and other oxidants measured in Claremont, California (Grosjean, 1983), are consistent with transport patterns. The recent work of Singh and Salas (1983) has shown that significant nighttime PAN concentrations can occur aloft, at least in a relatively clean environment. It is possible that the transport of PAN occurs aloft, as with ozone, and that under favorable conditions PAN can be transported long distances.

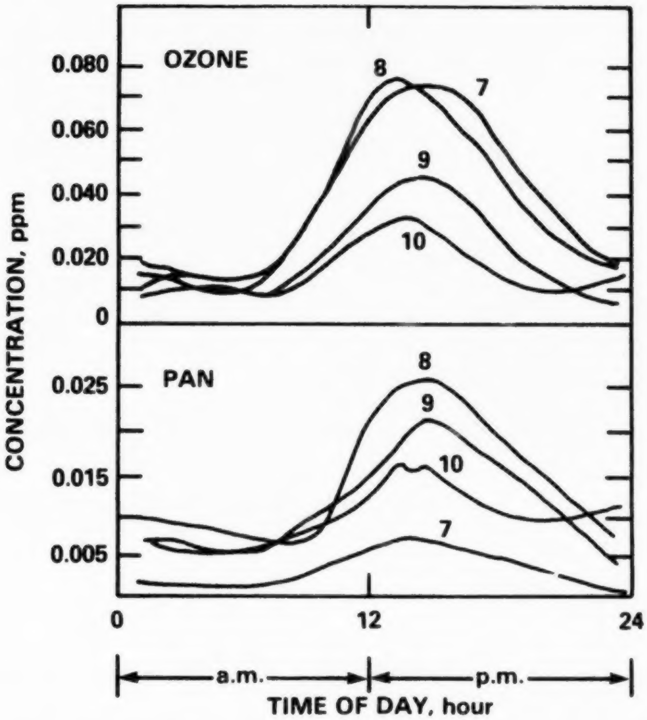

Figure 5-29. Average daily profile by month (July 7 - October 10) for PAN and ozone in New Brunswick, NJ, 1979. Numbers refer to months of the year.

Source: Lewis et al. (1983).

5.6.6.2 Intracity Variations. Few data on PAN concentrations at different sites in the same city are available. One study is available for Houston, Texas (Jorgen et al., 1978), in which PAN was measured on October 26 and 27, 1977, at three separate sites, two in Houston and one north of the city. Comparison of the levels of ozone and PAN peaks among the three sites on those 2 days reveals significant differences (Table 5-22). On October 26, the highest ozone concentrations (two peaks of 110 and 95 ppb at ~3:00 p.m. and ~7:00 p.m., respectively) were seen at site 3, in southeast Houston; while the highest PAN concentration on that day was a secondary peak of 15 ppb at ~8:00 p.m. at site 2 (mid-city). On October 27, the highest ozone concentration, 180 ppb, occurred at site 1, about 4 miles north-northeast of Houston, at ~1:00 p.m. That was accompanied at the same time by the highest PAN concentration for the day, 16 ppb.

Examination of Table 5-22 shows the lack of a consistent, quantitative relationship between PAN and ozone as indicated by intracity differences of more than twofold in ozone concentrations (afternoon peaks, sites 1 and 2, October 27) and differences of about fivefold in PAN concentrations between sites (afternoon peaks, sites 1 and 2, October 27).

5.6.6.3 Indoor-Outdoor Ratios of PAN Concentrations. No recent studies appear in the literature on indoor concentrations of PAN or indoor-outdoor ratios (I/O). In three school buildings in southern California, Thompson et al. (1973) found I/O ratios (expressed here as percentages) of 89, 97, and 148 percent, respectively, in the absence of air conditioning. With air conditioning, the I/O ratios were 75, 108, and 117 percent, respectively. Total oxidants were nearly constant all day, remaining about 30 percent (in air conditioning) of the average outside concentration. The higher I/O gradients for PAN than for oxidants were attributed by the authors to the greater breakdown of ozone ("oxidants") through its reaction with surfaces. The cooler temperatures indoors are the probable cause of the greater persistence of PAN indoors. Like ozone, PAN also decays indoors, but over an extended period (Thompson et al., 1973).

5.7 CONCENTRATIONS OF OTHER PHOTOCHEMICAL OXIDANTS IN AMBIENT AIR

Concentrations of nitrogen dioxide (NO_2) and related nitrogenous oxidants are presented in a recent criteria document on oxides of nitrogen (U.S. Environmental Protection Agency, 1982b) and are not given here. In addition, the

TABLE 5-22. INTRACITY VARIATIONS IN PEAK OZONE AND PAN CONCENTRATIONS IN HOUSTON, OCTOBER 26 AND 27, 1977

Site	Date	O_3, ppb	Time of peak	PAN, ppb	Time of peak
1 (~4 mi NNE of Houston)	10/26	75	1:00 p.m.	2	9:00 a.m. - 5:00 p.m. (plateau)
	10/27	180	2:00 p.m.	16	2:00 p.m.
2 (mid-city)	10/26	50	2:00-3:00 p.m.	2	2:00-6:00 p.m. (plateau)
	10/26	50	8:00 p.m.	10	7:00 p.m.
	10/27	70	1:00-3:00 p.m.	3	12:30-3:00 p.m.
3 (SE Houston)	10/26	110	3:00 p.m.	8	2:00 p.m.
	10/26	95	7:00 p.m.	12	5:30 p.m.
	10/27	90	1:00 p.m.	4	11:30 a.m.
	10/27	55	7:30 p.m.	4	6:30 p.m.

Source: Jorgen et al. (1978).

comprehensive review by Altshuller (1983) also documents available information on nitrogenous oxidants such as nitric acid (HNO_3) and peroxynitric acid, as well as on formic acid (HCOOH) and hydrogen peroxide (H_2O_2). The reader is referred to these reviews for information on these oxidants. The two non-nitrogenous oxidants, formic acid and hydrogen peroxide, are appropriate concerns for this document, however, and the limited information on concentrations of these two pollutants is summarized below.

Studies on the toxicologic effects of formic acid, though limited in number, have shown only negligible effects, even in animals exposed to levels as high as 20 ppm (aerosol vapor) (see Chapter 9). These levels are three orders of magnitude greater than the concentrations seen in polluted urban atmospheres. For example, maximum concentrations of HCOOH observed by Tuazon and coworkers, using FTIR (Tuazon et al., 1978; 1980; 1981b), in Claremont and Riverside, California, were in the range of 5 to 20 ppb in a study covering 5 years. The ranges of concentrations of HCOOH measured by Tuazon et al. were consistent with those found in a long-path FTIR study by Hanst et al. (1982). The FTIR method offers a reliable assessment of the ambient air concentrations of HCOOH and reported concentrations are believed to be accurate.

Data on HCOOH concentrations for 2 days in October 1978 are shown in Figure 5-30 (Tuazon et al., 1981b). The diurnal pattern is similar to that of related oxidants and of some of the other smog products.

The measurement of hydrogen peroxide (H_2O_2) in ambient air is fraught with difficulties that remain unresolved. Ozone itself is known to be an interference in virtually all of the past and current measurement methods for H_2O_2 (Chapter 4). In his review of non-ozone oxidants and other smog constituents and photochemical products, Altshuller (1983) examined data obtained in the South Coast Air Basin of California in the late 1970s and in 1980 for possible consistency in the interference of ozone in H_2O_2 measurements. Laboratory experiments (Heikes et al., 1982) have indicated that 1 ppb H_2O_2 would be generated per 100 ppb ozone. The analysis by Altshuller shows that this relationship does not hold in ambient air in the South Coast Air Basin once H_2O_2 levels exceed about 5 to 10 ppb; and Altshuller (1983) concluded that variations in H_2O_2 measurements there remain unexplained.

Because of measurement problems, the true levels of H_2O_2 in ambient air are unknown, especially in polluted areas, where multiple interferences may possibly occur. Attempts to detect hydrogen peroxide by means of FTIR spectroscopy have all been negative, even in polluted areas. The method can measure H_2O_2 in ambient air with specificity at H_2O_2 levels $\geq$ 40 ppb, which is the limit of detection for an FTIR instrument with a 1-km pathlength (see Chapter 4).

Notwithstanding measurement difficulties, some ranges of H_2O_2 concentrations at urban and nonurban sites have been reported in the literature. These are given in Table 5-23, along with the general type of measurement method used to obtain the reported concentrations. It must be kept in mind, however, that the reported concentrations, though they represent state-of-the-art measurements, are thought not to be accurate.

5.8 SUMMARY

In the context of this document, the concentrations of ozone and other photochemical oxidants found in ambient air are important for: (1) assessing potential exposures of human and other receptors; (2) determining the range of ambient air concentrations of ozone and other photochemical oxidants relative

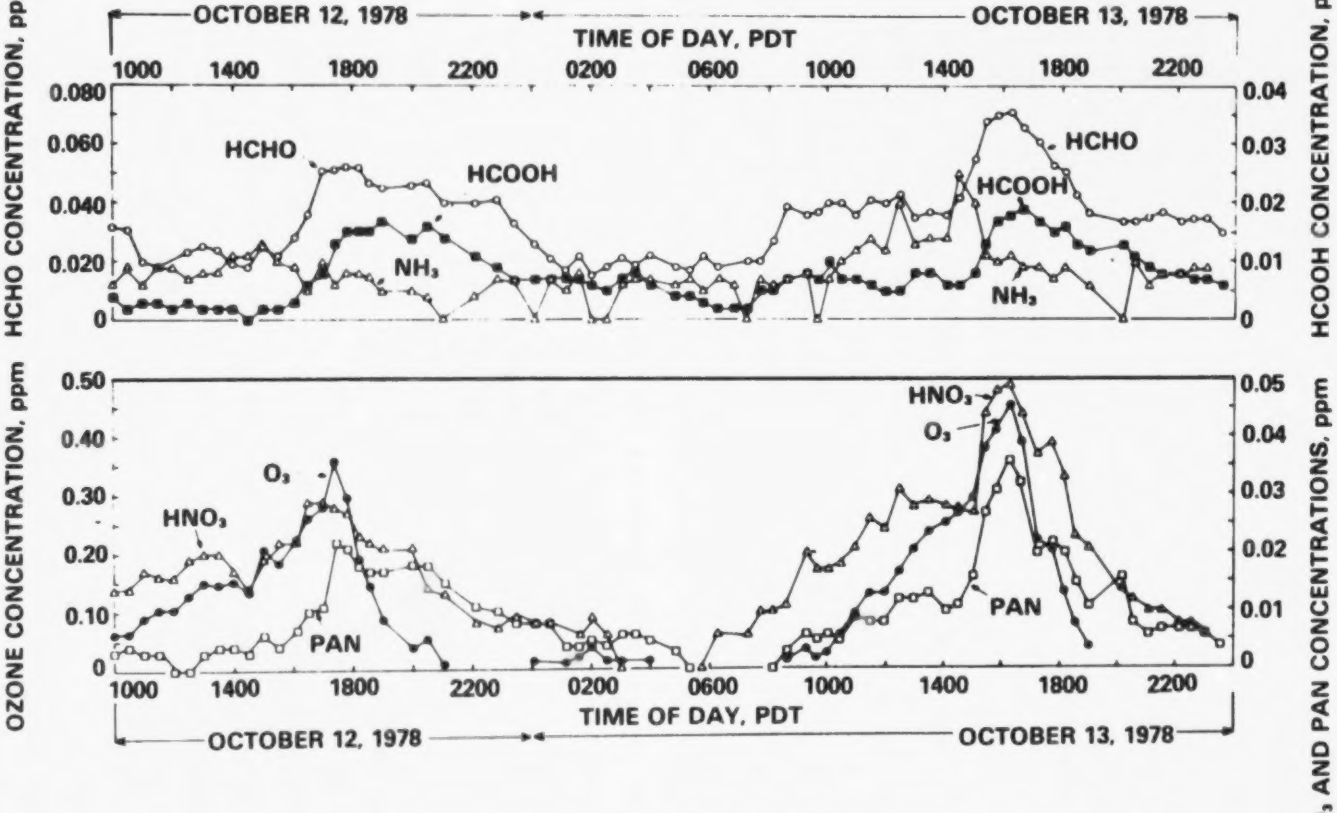

Figure 5-30. Diurnal profile of HCOOH, along with other oxidants and smog constituents, on October 12 and 13, 1978, at Claremont, CA.

Source: Tuazon et al. (1981b).

TABLE 5-23. CONCENTRATIONS[a] OF HYDROGEN PEROXIDE IN AMBIENT AIR AT URBAN AND NONURBAN SITES
(ppb)

Location	Date	Concns., and comments	Method	Reference
Hoboken, NJ (urban)	1970	≤ 40	Titanium (IV) sulfate/8-quinolinol	Bufalini et al. (1972)
Riverside, CA (urban)	1970	≤180 (during smog episode with 650 ppb oxidants)	Titanium (IV) sulfate/8-quinolinol	Bufalini et al. (1972)
Riverside and Claremont, CA (urban)	July-Aug. 1977	100 max. (ozone also 100 and increasing); 10 to 50 on most days	Luminol chemiluminescence	Kok et al. (1978)
Minneapolis, MN (urban)	NA[b]	≤6	Wet chemical[c]	Heikes et al. (1982)
Boulder, CO (urban)	NA	≤0.5	Wet chemical[c]	Heikes et al. (1982)
Boulder, CO (nonurban, east of Boulder)	Feb. 1978	0.2 to 3	Luminol chemiluminescence	Kelly et al. (1979)
Tucson, AZ (nonurban, 54 km SE of Tucson)	NA	≤7	Luminol chemiluminesence	Farmer and Dawson (1982)
Tucson, AZ (remote, near Tucson)	NA	~1	Luminol chemiluminescence	Farmer and Dawson (1982)

[a] Note: Since methods used to obtain these data are all subject to positive interference by ozone, data presented here are not reliable. They are included as a summary of reported concentrations.

[b] Not available.

[c] See Chapter 4 for method used by Heikes et al. (1982).

Source: Derived from data in Altshuller (1983).

to demonstrated "effects levels" (Chapters 6-12); (3) determining indoor-outdoor gradients for exposure analyses; (4) assessing whether the concentrations of oxidants other than ozone, singly, collectively, or in combination with ozone, are cause for concern; and (5) evaluating the adequacy of ozone as a control surrogate for other photochemical oxidants, if concentrations of the other oxidants are cause for concern given the effects and the "effects levels" of those oxidants.

5.8.1 Ozone Concentrations in Urban Areas

In Table 5-24, 1983 ozone concentrations for Standard Metropolitan Statistical Areas (SMSAs) having populations $\geq$ 1 million are given by geographic area, demarcated according to United States Census divisions and regions (U.S. Department of Commerce, 1982). The second-highest concentrations among daily maximum 1-hour values measured in 1983 in the 38 SMSAs having populations of at least 1 million ranged from 0.10 ppm in the Ft. Lauderdale, Florida; Philadelphia, Pennsylvania; and Seattle, Washington, areas to 0.37 ppm in the Los Angeles-Long Beach, California, area. The second-highest value among daily maximum 1-hour ozone concentrations for 35 of the 38 SMSAs in Table 5-24 equaled or exceeded 0.12 ppm. The data clearly show, as well, that the highest 1-hour ozone concentrations in the United States occurred in the northeast (New England and Middle Atlantic states), in the Gulf Coast area (West South Central states), and on the west coast (Pacific states). Second-highest daily maximum 1-hour concentrations in 1983 in the SMSAs within each of these three areas averaged 0.16, 0.17, and 0.21 ppm, respectively. It should be emphasized that these three areas of the United States are subject to those meteorological and climatological factors that are conducive to local oxidant formation, or transport, or both. It should also be emphasized that 9 of the 16 SMSAs in the country with populations $\geq$ 2 million are located in these areas.

Emissions of manmade oxidant precursors are usually correlated with population, especially emissions from area source categories such as transportation and residential heating (Chapter 3). Accordingly, when grouped by population, the 80 largest SMSAs had the following median values for their collective second-highest daily maximum 1-hour ozone concentrations in 1983: populations $\geq$ 2 million, 0.17 ppm O_3; populations of 1 to 2 million, 0.14 ppm O_3; and populations of 0.5 to 1 million, 0.13 ppm O_3. As noted above, however,

TABLE 5-24. SECOND-HIGHEST OZONE CONCENTRATIONS AMONG DAILY MAXIMUM 1-hr VALUES IN 1983 IN STANDARD METROPOLITAN STATISTICAL AREAS WITH POPULATIONS $\geq$ 1 MILLION, GIVEN BY CENSUS DIVISIONS AND REGIONS[a]

Division and region	SMSA	SMSA population, millions	Second-highest 1983 O_3 concn., ppm
Northeast			
New England	Boston, MA	>2	0.18
Middle Atlantic	Buffalo, NY	1 to <2	0.12
	Nassau-Suffolk, NY	>2	0.17
	Newark, NJ	1 to <2	0.25
	New York, NY/NJ	>2	0.19
	Philadelphia, PA/NJ	>2	0.10
	Pittsburgh, PA	>2	0.14
South			
South Atlantic	Atlanta, GA	>2	0.17
	Baltimore, MD	>2	0.19
	Ft. Lauderdale-Hollywood, FL	1 to <2	0.10
	Miami, FL	1 to <2	0.12
	Tampa-St. Petersburg, FL	1 to <2	0.14
	Washington, DC/MD/VA	>2	0.17
South			
West South Central	Dallas-Ft. Worth, TX	>2	0.16
	Houston, TX	>2	0.28
	New Orleans, LA	1 to <2	0.12
	San Antonio, TX	1 to <2	0.12
North Central			
East North Central	Chicago, IL	>2	0.17
	Detroit, MI	>2	0.17
	Cleveland, OH	1 to <2	0.15
	Cincinnati, OH/KY/IN	1 to <2	0.15
	Milwaukee, WI	1 to <2	0.18
	Indianapolis, IN	1 to <2	0.14
	Columbus, OH	1 to <2	0.12
West North Central	St. Louis, MO/IL	>2	0.18
	Minneapolis-St. Paul, MN/WI	>2	0.13
	Kansas City, MO/KS	1 to <2	0.13

TABLE 5-24 (cont'd). SECOND-HIGHEST OZONE CONCENTRATIONS AMONG DAILY MAXIMUM 1-hr VALUES IN 1983 IN STANDARD METROPOLITAN STATISTICAL AREAS WITH $\geq$ 1 MILLION, GIVEN BY CENSUS DIVISIONS AND REGIONS[a]

Division and region	SMSA	SMSA population, millions	Second-highest 1983 O_3 concn., ppm
West			
Mountain	Denver-Boulder, CO	1 to <2	0.14
	Phoenix, AZ	1 to <2	0.16
Pacific	Los Angeles-Long Beach, CA	>2	0.37
	San Francisco-Oakland, CA	>2	0.17
	Anaheim-Santa Ana-Garden Grove, CA	1 to <2	0.28
	San Diego, CA	1 to <2	0.20
	Seattle-Everett, WA	1 to <2	0.10
	Riverside-San Bernardino-Ontario, CA	1 to <2	0.34
	San Jose, CA	1 to <2	0.16
	Portland, OR/WA	1 to <2	0.12
	Sacramento, CA	1 to <2	0.15

[a] Standard Metropolitan Statistical Areas and geographic divisions and regions as defined by Statistical Abstract of the United States (U.S. Department of Commerce, 1982).

Source: U.S. Environmental Protection Agency (1984a).

coincident meteorology favorable for oxidant formation undoubtedly contributes to the apparent correlation between population and ozone levels.

Among all stations reporting valid ozone data ($\geq$ 75 percent of possible hourly values per year) in 1979, 1980, and 1981 (collectively, 906 station-years) in the United States, the median second-highest 1-hour ozone value was 0.12 ppm, and 5 percent of the stations reported second-highest 1-hour values $\geq$ 0.28 ppm.

A pattern of concern in assessing responses to ozone in human populations and in vegetation is the occurrence of repeated or prolonged multiday periods when the ozone concentrations in ambient air are in the range of those known to elicit responses (see Chapters 10 and 12). In addition, the number of days of respite between such multiple-day periods of high ozone is of possible consequence. Data show that repeated, consecutive-day exposures to or respites from specified concentrations are location-specific. At a site in Dallas, Texas, for example, daily maximum 1-hour concentrations were $\geq$ 0.06 ppm for 2 to 7 days in a row 37 times in a 3-year period (1979 through 1981). A concentration of $\geq$0.18 ppm was recorded at that site on only 2 single days, however, and no multiple-day recurrences of that concentration or greater were recorded over the 3-year period. At a site in Pasadena, California, daily maximum 1-hour concentrations $\geq$0.18 ppm recurred on 2 to 7 consecutive days 33 times in that same 3-year period (1979 through 1981) and occurred, as well, on 21 separate days. These and other data demonstrate the occurrence in some urban areas of multiple-day potential exposures to relatively high concentrations of ozone.

5.8.2. Trends in Nationwide Ozone Concentrations

Trends in ozone concentrations nationwide are important for estimating potential exposures in the future of human populations and other receptors, as well as for examining the effectiveness of abatement programs. The determination of nationwide trends requires the application of statistical tests to comparable, representative, multiyear aerometric data. The derivation of recent trends in ozone concentrations and the interpretation of those trends is complicated by two potentially significant factors that have affected aerometric data since 1979: (1) the promulgation by EPA in 1979 of a new calibration procedure for ozone monitoring (see Chapter 4); and (2) the introduction by EPA of a quality-assurance program that has resulted in improved data-quality audits. The effects of these factors on ozone concentration measurements are superimposed on the effects on concentrations of any changes in meteorology or in precursor emission rates that may have occurred over the same time span.

The nationwide trends in ozone concentrations for a 9-year period, 1975 through 1983, are shown in Figure 5-31 (U. S. Environmental Protection Agency, 1984a). The data given are trends as gauged by the composite average of the second-highest value among daily maximum 1-hour ozone concentrations. Data from four subsets of monitoring stations, most of them urban stations, are given: (1) California stations only; (2) all stations except those in California; (3) all stations including those in California; and (4) all National Air Monitoring Stations (NAMS), which report data directly to EPA. Only stations reporting $\geq$ 75 percent of possible hourly values in the respective years are represented in the data.

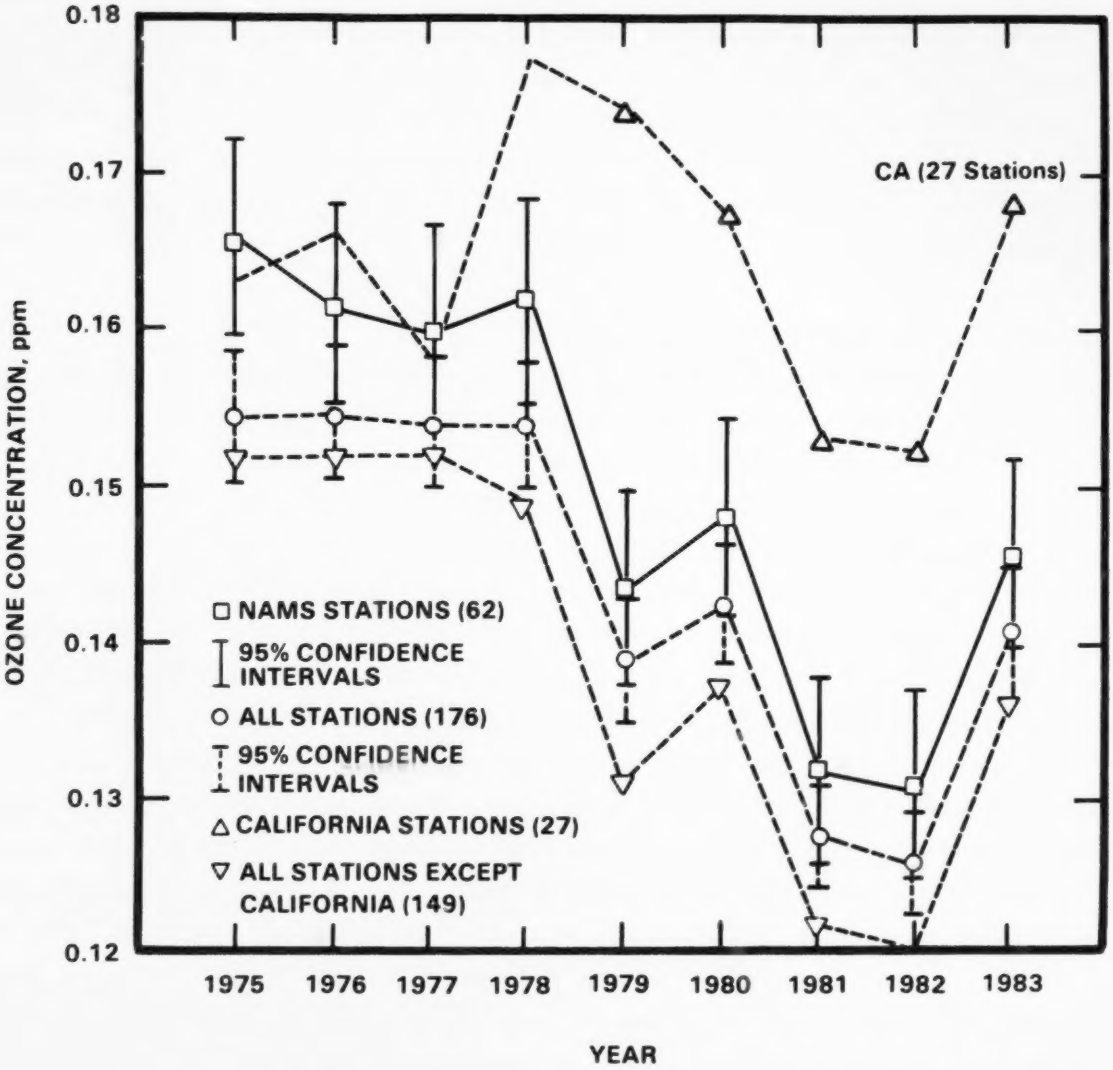

Figure 5-31. National trend in composite average of the second highest value among daily maximum 1-hour ozone concentrations at selected groups of sites, 1975 through 1983.

Source: U.S. Environmental Protection Agency (1984a).

For the entire 9-year period, 1975 through 1983, all subsets of monitoring stations show a decline in the composite second-highest daily maximum 1-hour ozone concentration. Between 1979, when the new, more accurate calibration procedure was promulgated, and 1982, a small decline of 9 to 10 percent in nationwide ozone concentrations occurred. From 1982 to 1983, however, concentrations increased by about 10 percent in California, by about 14 percent outside California, and by about 12 percent nationwide (all states). Recently published data for 1984 from a somewhat smaller number of sites (163) (U.S. Environmental Protection Agency, 1986) show a decrease in nationwide ozone concentrations from 1983 to 1984, with 1984 levels approximating those recorded in 1981. The portion of the apparent decline in ozone nationwide from 1975 through 1984 that is attributable to the calibration change of 1979 cannot be determined by simply applying a correction factor to all data, since not all monitoring stations began using the UV calibration procedure in the same year.

Figure 5-32 shows the nationwide frequency distributions of the first-, second-, and third-highest 1-hour O_3 concentrations at predominantly urban stations aggregated for 1979, 1980, and 1981, as well as the highest 1-hour O_3 concentration at site of the National Air Pollution Background Network (NAPBN) aggregated for the same 3 years. As shown by Figure 5-32, 50 percent of the second-highest 1-hour values from non-NAPBN sites in this 3-year period were 0.12 ppm or less and about 10 percent were equal to or greater than 0.20 ppm. At the NAPBN sites, the collective 3-year distribution (1979 through 1981) is such that about 6 percent of the values are less than 0.10 ppm and fewer than 20 percent are higher than 0.12 ppm.

5.8.3. Ozone Concentrations in Nonurban Areas

Few nonurban areas have been routinely monitored for ozone concentrations. Consequently, the aerometric data base for nonurban areas is considerably less substantial than for urban areas. Data are available, however, from two special-purpose networks, the National Air Pollution Background Network (NAPBN) and the Sulfate Regional Experiment network (SURE). Data on maximum 1-hour concentrations and arithmetic mean 1-hour concentrations reveal that maximum 1-hour concentrations at nonurban sites classified as rural (SURE study, Martinez and Singh, 1979; NAPBN studies, Evans et al., 1983) can sometimes exceed the concentrations observed at sites classified as suburban (SURE study, Martinez and Singh, 1979). For example, maximum 1-hour ozone concentrations measured in 1980 at Kisatchie National Forest (NF), Louisiana; Custer

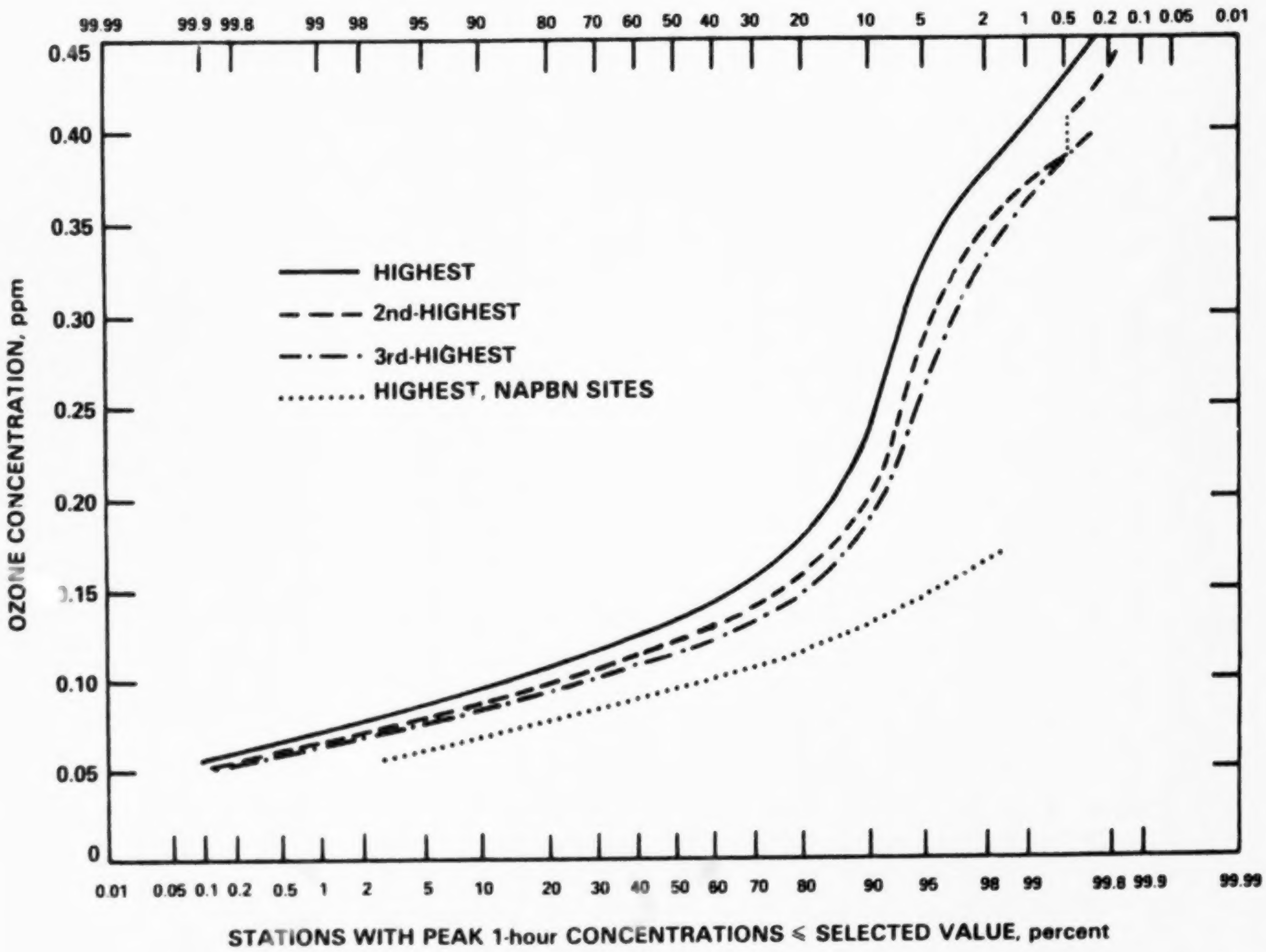

Figure 5-32. Distributions of the three highest 1-hour ozone concentrations at valid sites (906 station-years) aggregated for 3 years (1979, 1980, and 1981) and the highest ozone concentrations at NAPBN sites aggregated for those years (24 station-years).

Source: U.S. Environmental Protection Agency (1980, 1981, 1982).

NF, Montana; and Green Mt. NF, Vermont, were 0.105, 0.070, and 0.115 ppm, respectively. Arithmetic mean 1-hour concentrations for 1980 were 0.028, 0.037, and 0.032 ppm at the respective sites. For four nonurban (rural) sites in the SURE study, maximum 1-hour ozone concentrations were 0.106, 0.107, 0.117, and 0.153; and mean 1-hour concentrations ranged from 0.021 to 0.035 ppm. At the five nonurban (suburban) sites of the SURE study, maximum concentrations were 0.077, 0.099, 0.099, 0.080, and 0.118 ppm, respectively. The mean 1-hour concentrations at those sites were 0.023, 0.030, 0.025, 0.020, and 0.025 ppm, respectively.

Ranges of concentrations and the maximum 1-hour concentrations at some of the NAPBN and SURE sites show the probable influence of ozone transported from urban areas. In one documented case, for example, a 1-hour peak ozone concentration of 0.125 ppm at an NAPBN site in Mark Twain National Forest, Missouri, was measured during passage of an air mass whose trajectory was calculated to have included Detroit, Cincinnati, and Louisville in the preceding hours (Evans et al., 1983).

The second-highest concentration among all the daily maximum 1-hour concentrations measured at the NAPBN sites appear to be about one-half the corresponding concentrations measured at urban sites in the same years. No trend in concentrations at these NAPBN sites is discernible in the data record for 1979 through 1983.

These data corroborate the conclusion given in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) regarding urban-nonurban and urban-suburban gradients; i.e., nonurban areas may sometimes sustain higher peak ozone concentrations than those found in urban areas.

5.8.4. Diurnal and Seasonal Patterns in Ozone Concentrations

Since the photochemical reactions of precursors that result in ozone formation are driven by sunlight, as well as by emissions, the patterns of ozone occurrence in ambient air depend on daily and seasonal variations in sunlight intensity. The typical diurnal pattern of ozone in ambient air has a minimum ozone level around sunrise (near zero in most urban areas), increasing through the morning to a peak concentration in early afternoon, and decreasing toward minimal levels again in the evening. The 1978 criteria document ascribed the daily ozone pattern to three simultaneous processes: (1) downward transport of ozone from layers aloft; (2) destruction of ozone through contact with surfaces and through reaction with nitric oxide (NO) at ground level; and (3) *in situ* photochemical production of ozone (U.S. Environmental Protection Agency, 1978; Coffey et al., 1977; Mohnen, 1977; Reiter, 1977a). Obviously, meteorology is a controlling factor; if strong winds disperse the precursors or heavy clouds intercept the sunlight, high ozone levels will not develop. Another important variation on the basic diurnal pattern appears in some localities as a secondary peak in addition to the early afternoon peak. This secondary peak may occur any time from midafternoon to the middle of the night and is attributed to ozone transported from upwind areas where high ozone levels have occurred earlier in the day. Secondary peak concentrations can be higher than concentrations resulting from the photochemical reactions of locally emitted precursors (Martinez and Singh, 1979). At one nonurban site in Massachusetts (August 1977), for example, primary peak concentrations of about 0.11, 0.14, and 0.14 occurred at noon, from noon to about 4:00 p.m., and at noon, respectively, on 3 successive days of high ozone levels (Martinez and Singh, 1979). Secondary peaks at the same site for those same 3 days were about 0.150, 0.157, and 0.130 ppm at about 6:00 p.m., 8:00 p.m., and 8:00 p.m., respectively (Martinez and Singh, 1979).

Because weather patterns, ambient temperatures, and the intensity and wavelengths of sunlight all play important roles in oxidant formation, strong seasonal as well as diurnal patterns exist. The highest ozone levels generally occur in the spring and summer (second and third quarters), when sunlight reaching the lower troposphere is most intense and stagnant meteorological conditions augment the potential for ozone formation and accumulation. Average summer afternoon levels can be from 150 to 250 percent of the average winter afternoon levels. Minor variations in the smog season occur with location, however. In addition, it is possible for the maximum and second-highest 1-hour ozone concentration to occur outside the two quarters of highest average ozone concentrations. Exceptions to seasonal patterns are potentially important considerations with regard to the protection of crops from ozone damage, especially since respective crops have different growing seasons in terms of length, time of year, and areas of the country in which they are grown.

In addition to the seasonal meteorological conditions that obtain in the lower troposphere, stratospheric-tropospheric exchange mechanisms exist that produce relatively frequent but sporadic, short-term incursions into the troposphere of stratospheric ozone (see Chapter 3). Such incursions show a seasonal pattern, usually occurring in late winter or early spring.

Percentile distributions, by season of the year, of concentration data from all eight NAPBN sites show that the arithmetic mean 1-hour concentration (averaged over a minimum of 3 years of data at each site, for 1977 through 1983) was higher in the second quarter of the year (April, May, June) at seven of the eight stations; and was only negligibly lower than the third-quarter value at the eighth station. The maximum 1-hour concentrations at respective sites, aggregated over 3 to 6 years, depending on the data record for each site, ranged from 0.050 ppm at Custer NF, MT (in the fourth quarter) to 0.155 ppm at Mark Twain NF, MO (in the third quarter). The second-highest 1-hour concentration among maximum daily 1-hour values ranged from 0.050 ppm at Custer NF, MT (in the fourth quarter), to 0.150 ppm at Mark Twain NF, MO (in the third quarter). The data also show that 99 percent of the 1-hour concentrations measured were well below 0.12 ppm, even in the second quarter of the year, when incursions of stratospheric ozone are expected to affect, at least to some degree, the concentrations measured at these stations. Excursions above 0.12 ppm were recorded in 1979 and 1980 at NAPBN sites; but none were recorded in 1981 (Evans et al., 1983; Lefohn, 1984).

Because of the diurnal patterns of ozone, averaging across longer-term periods such as a month, a season, or longer masks the occurrence of peak concentrations (see, e.g., Lefohn and Benedict, 1985). This is an obvious and familiar statistical phenomenon. It is pointed out, however, because it has direct relevance to the protection of public health and welfare. Averaging times must correspond to, or be related in a consistent manner to, the pattern of exposure that elicits untoward responses.

5.8.5 Spatial Patterns in Ozone Concentrations

In addition to temporal variations, both macro- and microscale spatial variations in ozone concentrations occur that have relevance ranging from important to inconsequential for exposure assessments. Differences in concentrations or patterns of occurrence, or both, are known to exist, for example, between urban and nonurban areas, between indoor and outdoor air, within large metropolises, and between lower and higher elevations. The more important variations are summarized below.

5.8.5.1 Urban-Nonurban Differences in Ozone Concentrations. Ozone concentrations differ between urban and rural, between urban and remote, and even between rural and remote sites, as discussed in part in the preceding section on temporal variations. The variations with area and type of site are variations both in the timing and the magnitude of the peak concentrations, and, in the case of transported ozone, are related to the temporal variations between urban and nonurban areas discussed above. Data from urban, suburban, rural, and remote sites (see, e.g., SAROAD, 1985a-f; Martinez and Singh, 1979; Lefohn, 1984; Evans, 1985; respectively) corroborate the conclusion drawn in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) that ozone concentrations can sometimes be higher in some suburban or even rural areas downwind of urban plumes than in the urban areas themselves; and, furthermore, that higher concentrations can persist longer in rural and remote areas, largely because of the absence of nitric oxide (NO) for chemical scavenging.

In nonurban areas downwind of urban plumes, peak concentrations can occur, as the result of transport, at virtually any hour of the day or night, depending upon many factors, such as the strength of the emission source, induction time, scavenging, and wind speed (travel time) and other meteorological factors. The dependence of the timing of peak exposures upon these transport-related factors is well-known and is illustrated here by two studies. Evans et al. (1983) calculated multiday trajectories for air parcels reaching a nonurban sites in the Mark Twain National Forest, Missouri, during an episode. Four separate trajectories, all of which passed over the Ohio River Valley and the Great Lakes region, impacted the forest site at different times in a 24-hour period (in which the maximum 1-hour concentration measured was 0.125 ppm). Subsequently, regional cloud cover and rains produced shifts in air flow and also reduced the potential for ozone formation, alleviating the impact at the site. Kelly et al. (1986) showed in the Detroit area that peak ozone concentrations occurred at distances of 10 to 70 km (ca. 6 to 43 mi) north-northeast of the urban center. Consequently, it would be possible for peak ozone concentrations to occur in the late afternoon or early evening in nonurban areas downwind of Detroit. Kelly et al. (1986) also found that concentrations diminished again beyond 70 km (ca. 43 mi) downwind of the urban center. Thus, as illustrated by these and similar data, beyond the distance traversed in the time required for maximum ozone formation in an urban plume, ozone concentrations will decrease (unless fresh emissions are injected into the plume) as the rate of ozone formation decreases, the plume disperses, surface deposition or other scavenging occurs, and meteorological conditions intervene.

It is not surprising, therefore, that in rural areas lying beyond the point of maximum ozone formation, for a given set of conditions, peak concentrations are lower and average diurnal profiles are flatter than in urban and near-urban areas (see, e.g., SAROAD, 1985b-f, for rural and remote sites). In remote areas beyond the influence of urban plumes, average peak concentrations will be still lower and average diurnal profiles still flatter (see e.g., Evans, 1985). Exceptions to these generalizations occur, of course, because of the complex interactions of topography, meteorology, and photochemistry.

Such temporal and spatial differences between ozone concentrations in urban versus nonurban areas are important considerations for accurately assessing actual and potential exposures for human populations and for vegetation in nonurban areas, especially since the aerometric data for nonurban areas are far from abundant.

5.8.5.2 Geographic, Vertical, and Altitudinal Variations in Ozone Concentrations.

Although of interest and concern when estimating global ozone budgets, demonstrated variations in ozone concentrations with latitude and the lesser variations with longitude have little practical significance for assessing exposure within the contiguous United States. The effects on ozone concentrations of latitude and longitude within the contiguous states are minor, and are reflected in the aerometric data bases. Of more importance, ozone concentrations are known to increase with increasing height above the surface of the earth. Conversely, they may be viewed as decreasing with proximity to the surface of the earth, since the earth's surface acts as a sink for ozone (see, e.g., Seiler and Fishman, 1981; Galbally and Roy, 1980; Oltmans, 1981, cited in Logan et al., 1981). The most pertinent vertical and altitudinal gradients in ozone concentrations are: (1) increases in concentration with height above the surface of the ground (regardless of altitude); (2) increases in concentration with altitude; and (3) variations in concentrations with elevation in mountainous areas, attributable to transport and overnight conservation of ozone aloft, nocturnal inversions, trapping inversions, upslope flows, and other, often location-specific interactions between topography, meteorology, and photochemistry.

The importance of monitoring concentrations at the proper height above the surface of the ground has been known for a long time, and EPA guidance on the placement of monitoring instruments (see Chapter 4) is predicated on the existence of a vertical gradient as ozone is depleted by reaction with ground-level emissions of NO or by deposition on reactive surfaces such as vegetation. Data illustrative of the near-surface gradient were reported by Pratt et al. (1983), who measured ozone concentrations at two separate heights (3 and 9 or 6 and 9 meters) above the ground at three rural, vegetated sites. Although the maximum mean difference between 3 and 9 meters was 3 ppb, this difference was similar to the mean difference between sites at the same height. Given the height of some vegetation canopies, especially forests, even such small differences over a spread of 6 meters should probably be taken into consideration when interpreting reported dose-response functions.

The gradual increase in ozone concentrations with altitude has been documented by a number of workers (see e.g., Viezee et al., 1979; Seiler and Fishman, 1981; Oltmans, 1981, as cited in Logan et al., 1981). There is a general increase in concentration with altitude, but as described by Seiler and Fishman (1981) and Oltmans (1981; cited in Logan et al., 1981), for example, two relatively pronounced gradients exist, one between the surface of the earth and 2 km (ca. 1 mi) and one even more pronounced between 8 and 12 km (ca. 5 and 7.5 mi).

Increases in concentrations with altitude could potentially be of some consequence for passengers and airline personnel on high-altitude flights in the absence of adequate ventilation-filtration systems (see Chapter 11). Variations with height above the surface and with elevation, in mountainous areas, however, should be taken into account to ensure the accurate assessment of exposures and the accurate derivation of dose-response functions, especially for forests and other vegetation.

Variations in ozone concentrations with elevation, not always consistent or predictable, have been reported by researchers investigating the effects of ozone on the mixed-conifer forest ecosystem of the San Bernardino Mountains of California. Measurements taken at four monitoring stations at four different elevations showed that peak ozone concentrations occurred progressively later in the day at progressively higher elevations (Miller et al., 1972). Ozone concentrations >0.10 ppm occurred for average durations of 9, 13, 9, and

8 hr/day at the four respective stations, going from lower to higher elevations. The occurrence for 13 hr/day of concentrations >0.10 ppm at the station at 817 m (2860 ft) was probably the result of contact of that zone of the mountainside with the inversion layer (U.S. Environmental Protection Agency, 1978). Nighttime concentrations rarely decreased below 0.05 ppm at the mountain crest; whereas at the lowest elevation, the basin station at 442 m (1459 ft), the nighttime concentration usually decayed to near zero. Trapping inversions were major contributors to the elevational gradients observed in this study, which was conducted in the 1970s. Oxidant concentrations within the inversion were found not to be uniform but to occur in multiple layers and strong vertical gradients. The important result of the trapping of oxidants in the inversion layers was the prolonged contact of high terrain with oxidants at night (U.S. Environmental Protection Agency, 1978).

In a more recent report, Wolff et al. (1986) described measurements made in July 1975 at three separate elevations at High Point Mountain in northeastern New Jersey. The daily ozone maxima were similar at different elevations. At night, however, ozone concentrations were nearly zero in the valley but increased with elevation on the mountainside. Greater cumulative doses (number of hours at >0.08 ppm) were sustained at the higher elevations, 300 and 500 m, respectively (ca. 990 and 1650 ft, respectively). Wolff et al. (1986) related this phenomenon to the depth of the nocturnal inversion layer and the contact with the mountainside of ozone conserved aloft at night.

These concentration gradients with increased elevation are important for accurately describing concentrations at which injury or damage to vegetation, especially forests, may occur. Researchers investigating the effects of ozone on forest ecosystems have seldom measured nighttime ozone concentrations because the stomates of most species are thought to be closed at night, thus preventing the internal flux of ozone that produces injury or damage (see Chapter 6). If stomates remain even partially open at night, however, the possible occurrence of nighttime peak concentrations of ozone, the occurrence of multiple peaks in a 24-hour period, or the persistence of elevated concentrations that do not decay to near zero overnight should not be overlooked. Furthermore, the lack of NO for nighttime scavenging in nonurban areas and the persistence of ozone overnight at higher elevations will result in the presence of relatively higher concentrations in such areas at sunrise when the stomates open and photosynthesis begins. This possibility requires that exposure assessments, in the absence of sufficient aerometric data for forests and other vegetated areas, take such factors into consideration.

5.8.5.3 Other Spatial Variations in Ozone Concentrations. Other spatial variations are important for exposure assessments for human populations. Indoor-outdoor gradients in ozone concentrations are known to occur even in buildings or vehicles ventilated by fresh air rather than air conditioning (e.g., Sabersky et al., 1973; Thompson et al., 1973; Peterson and Sabersky, 1975). Ozone reacts with surfaces inside buildings, so that decay may occur fairly rapidly, depending upon the nature of interior surfaces and furnishings (e.g., Davies et al., 1984; Contant et al., 1985). Ratios of indoor-to-outdoor (I/O) ozone concentrations are quite variable, however, since cooling and ventilation systems, air infiltration or exchange rates, interior air circulation rates, and the composition of interior surfaces all affect indoor ozone concentrations. Ratios (I/O, expressed as percentages) in the literature thus vary from 100 percent in a non-air-conditioned residence (Contant et al., 1985); to 80 ± 10 percent (Sabersky et al., 1973) in an air-conditioned office building (but with 100 percent outside air intake); to 10 to 25 percent in air-conditioned residences (Berk et al., 1981); and to as low as near zero in air-conditioned residences (Stock et al., 1983; Contant et al., 1985).

On a larger scale, within-city variations in ozone concentrations can occur, even though ozone is a "regional" pollutant. Data show, for example, relatively homogeneous ozone concentrations in New Haven, Connecticut (SAROAD, 1985a), a moderately large city that is downwind of a reasonably well-mixed urban plume (Wolff et al., 1975; Cleveland et al.; 1976a,b). In a large metropolis, however, appreciable gradients in ozone concentrations can exist from one side of the city to the other, as demonstrated for New York City (Smith, 1981), and for Detroit (Kelly et al., 1986). Such gradients should be taken into consideration, where possible, in exposure assessments.

5.8.6 Concentrations and Patterns of Other Photochemical Oxidants

5.8.6.1 Concentrations. No aerometric data are routinely obtained by Federal, state, or local air pollution agencies for any photochemical oxidants other than nitrogen dioxide and ozone. The concentrations presented in this document for non-ozone oxidants were all obtained in special field investigations. The limitations in the number of locations and areas of the country represented in the information presented simply reflect the relative paucity of data in the published literature.

The four non-ozone photochemical oxidants for which at least minimal concentration data are available are formic acid, peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and hydrogen peroxide (H_2O_2). Peroxybenzoyl nitrate has not been clearly identified in ambient air in the United States.

The highest concentrations of PAN reported in the older literature, 1960 through the present, were those found in the Los Angeles area: 70 ppb (1960), 214 ppb (1965); and 68 ppb (1968) (Renzetti and Bryan, 1961; Mayrsohn and Brooks, 1965; Lonneman et al., 1976; respectively).

The highest concentrations of PAN measured and reported in urban areas in the past 5 years were 42 ppb at Riverside, California, in 1980 (Temple and Taylor, 1983) and 47 ppb at Claremont, California, also in 1980 (Grosjean 1981). These are clearly the maximum concentrations of PAN reported for California and for the entire country in this period. Other maximum PAN concentrations measured in the last decade in the Los Angeles Basin have been in the range of 11 to 37 ppb. Average concentrations of PAN in the Los Angeles Basin in the past 5 years have ranged from 4 to 13 ppb (Tuazon et al., 1981a; Grosjean, 1983; respectively). The only published study covering urban PAN concentrations outside California in the past 5 years is that of Lewis et al. (1983) for New Brunswick, New Jersey, in which the average PAN concentration was 0.5 ppb and the maximum was 11 ppb during September 1978 through May 1980. Studies outside California from the early 1970s through 1978 showed average PAN concentrations ranging from 0.4 ppb in Houston, Texas, in 1976 (Westberg et al., 1978) to 6.3 ppb in St. Louis, Missouri, in 1973 (Lonneman et al., 1976). Maximum PAN concentrations outside California for the same period ranged from 10 ppb in Dayton, Ohio, in 1974 (Spicer et al., 1976) to 25 ppb in St. Louis (Lonneman et al., 1976).

The highest PPN concentration reported in studies over the period 1963 through the present was 6 ppb in Riverside, California (Darley et al., 1963). The next highest reported PPN concentration was 5 ppb at St. Louis, Missouri, in 1973 (Lonneman et al., 1976). Among more recent data, maximum PPN concentrations at respective sites ranged from 0.07 ppb in Pittsburgh, Pennsylvania, in 1981 (Singh et al., 1982) to 3.1 ppb at Staten Island, New York (Singh et al., 1982). California concentrations fell within this range. Average PPN concentrations at the respective sites for the more recent data ranged from 0.05 ppb at Denver and Pittsburgh to 0.7 ppb at Los Angeles in 1979 (Singh et al., 1981).

Altshuller (1983) has succinctly summarized the nonurban concentrations of PAN and PPN by pointing out that they overlap the lower end of the range of urban concentrations at sites outside California. At remote locations, PAN and PPN concentrations are lower than even the lowest of the urban concentrations by a factor of 3 to 4.

The concentrations of H_2O_2 reported in the literature to date must be regarded as inaccurate since ozone is now thought to be an interference in all methods used to date except FTIR (Chapter 4). Measurements by FTIR, the most specific and accurate method now available, have not demonstrated unambiguously the presence of H_2O_2 in ambient air, even in the high-oxidant atmosphere of the Los Angeles area. (The limit of detection for a 1-km-pathlength FTIR system is around 0.04 ppm.)

Recent data indicate the presence in urban atmospheres of only trace amounts of formic acid: $\leq$ 15 ppb, measured by FTIR (Tuazon et al., 1981b). Estimates in the earlier literature (1950s) of 600 to 700 ppb of formic acid in smoggy atmospheres were erroneous because of faulty measurement methodology (Hanst et al., 1982).

5.8.6.2 Patterns. The patterns of formic acid (HCOOH), PAN, PPN, and H_2O_2 may be summarized fairly succinctly. Qualitatively, diurnal patterns are similar to those of ozone, with peak concentrations of each of these occurring in close proximity to the time of the ozone peak. The correspondence in time of day is not exact, but is close. As demonstrated by the work of Tuazon et al. (1981b), ozone concentrations return to baseline levels somewhat faster than the concentrations of PAN, HCOOH, or H_2O_2 (PPN was not measured).

Seasonally, winter concentrations (third and fourth quarters) of PAN are lower than summer concentrations (second and third quarters). The percentage of PAN concentrations (PAN/O_3 x 100) relative to ozone, however, is higher in winter than in summer. Data are not readily available on the seasonal patterns of the other non-ozone oxidants.

Indoor-outdoor data on PAN are limited to one report (Thompson et al., 1973), which confirms the pattern to be expected from the known chemistry of PAN; that is, it persists longer indoors than ozone. Data are lacking on indoor-outdoor ratios for the other non-ozone oxidants.

5.8.7 Relationship Between Ozone and Other Photochemical Oxidants

The relationship between ozone concentrations and the concentrations of PAN, PPN, H_2O_2, and HCOOH is important only if these non-ozone oxidants are shown to produce potentially adverse health or welfare effects, singly, in combination with each other, or in various combinations with ozone at concentrations correponding to those found in ambient air. If only ozone is shown to produce adverse health or welfare effects in the concentration ranges of concern, then only ozone must be controlled. If any or all of these other four oxidants are shown to produce potentially adverse health or welfare effects, at or near levels found in ambient air, then such oxidants will also have to be controlled. Since ozone and all four of the other oxidants arise from reactions among the same organic and inorganic precursors, an obvious question is whether the control of ozone will also result in the control of the other four oxidants.

Controlled-exposure studies on these non-ozone oxidants have employed concentrations much higher than those found in ambient air (see Chapters 9 and 10). Because PAN may have contributed, however, to the eye irritation symptoms reported in earlier epidemiological studies, and because PAN is the most abundant of these non-ozone oxidants, the relationship between ozone and PAN concentrations in ambient air remains of interest.

The patterns of PAN and ozone concentrations are not quantitatively similar but do show qualitative similarities for most locations at which both pollutants have been measured in the same study. That a quantitative, monotonic relationship between ozone and PAN is lacking, however, is shown by the range of PAN-to-ozone ratios, expressed as percentages, between locations and at the same location, as reported in the review of Altshuller (1983).

Certain other information bears out the lack of a monotonic relationship between PAN and ozone. Not only are PAN-ozone relationships not consistent between different urban areas, but they are not consistent in urban versus nonurban areas, in summer versus winter, in indoor versus outdoor environments, or even, as the data show, in location, timing, or magnitude of diurnal peak concentrations within the same city. Data obtained in Houston by Jorgen et al. (1978), for example, show variations in peak concentrations of PAN and in relationships to ozone concentrations of those peaks among three separate monitoring sites. Temple and Taylor (1983) have shown that PAN concentrations are a greater percentage of ozone concentrations in winter than in the remainder of the year in California. Lonneman et al. (1976) demonstrated that PAN, absolutely and as a percentage of ozone, is considerably lower in nonurban than in urban areas. Thompson et al. (1973), in what is apparently the only published report on indoor concentrations of PAN, showed that PAN persists longer than ozone indoors. (This is to be expected from its enhanced stability at cooler-than-ambient temperatures such as found in air-conditioned buildings.) Tuazon et al. (1981b) demonstrated that PAN persists in ambient air longer than ozone, its persistence paralleling that of nitric acid, at least in the locality studied (Claremont, CA). Reactivity data presented in the 1978 criteria document for ozone and other photochemical oxidants indicated that all precursors that give rise to PAN also give rise to ozone. The data also showed, however, that not all precursors giving rise to ozone also give rise to PAN, and that not all that give rise to both are equally reactive toward both, with some precursors preferentially giving rise, on the basis of units of product per unit of reactant, to more of one product than the other (U.S. Environmental Protection Agency, 1978).

In the review cited earlier, Altshuller (1983) examined the relationships between ozone and a variety of other smog components, including PAN, PPN, H_2O_2, HCOOH, aldehydes, aerosols, and nitric acid. He concluded that "the ambient air measurements indicate that ozone may serve directionally, but cannot be expected to serve quantitatively, as a surrogate for the other products" (Altshuller, 1983). It must be emphasized that the issue Altshuller examined was whether ozone could serve as an abatement surrogate for all photochemical products, not just the subset of non-ozone oxidants of concern in this document. Nevertheless, a review of the data presented indicates that his conclusion is applicable to the non-ozone oxidants examined in this document.

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